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This report provides information that can be used by environmental regulatory agencies and others as a source of technical information describing waste management options for solvents and other wastes containing low molecular weight organic compounds. These options include waste minimization (i.e., source reduction, reuse, recycling), treatment and disposal of waste streams. Although emphasis is placed on the collection and interpretation of performance data for proven technologies, the full range of waste minimization processes and treatment/recovery technologies that can be used to manage solvent wastes is discussed.

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CONTENTS

Acknowledgement iii
Figures vi
Tables . . . .
Project Summary 1

1. Introduction 1-1
2. Background 2-1
    Schedule for Land Disposal Prohibition 2-1
    Treatment Standards for Certain Solvents 2-3
3. Current Industrial Sources, Generation, and Management Activities for Solvent Wastes 3-1
    Industrial Sources of Waste Solvents 3-1
    Solvent Waste Generation 3-22
    Waste Management Practices 3-30
4. Commercial Offsite Recycling, Treatment, and Disposal Capacity 4-1
    Commercial Solvent Recycling Industry 4-1
    Available Recycling Treatment and Disposal Capacity 4-9
5. Waste Minimization Processes and Practices 5-1
    Source Reduction 5-1
    Recycling/Reuse 5-11
    Additional Examples of Waste Minimization Practices 5-31
6. Pretreatment 6-1
    Liquids Containing Suspended or Floating Materials 6-3
    Solid/Sludge Wastes Containing Liquids 6-5
    Inorganic Solid Wastes Containing Low Levels of Organics . 6-5
    Bulky, Non-Uniform Solid Wastes 6-7
    Low Heat Content or Low Viscosity Liquids 6-8
7. Physical Treatment Processes 7-1
    Distillation 7-3
    Evaporation Processes 7-48
    Steam Stripping 7-88
    Air Stripping 7-134
    Liquid - Liquid Extraction 7-153
    Carbon Adsorption 7-184
    Resin Adsorption 7-223
8. Chemical Treatment Processes 8-1
    Wet Air Oxidation 8-2
    Supercritical Fluid Oxidation 8-31
    Ozonation 8-47
    Other Chemical Oxidation Processes 8-63
    Chlorinolysis Processes 8-75
    Chemical Dechlorination 8-86

CONTENTS (continued)

9. Biological Methods 9-1
    Process Description 9-1
    Demonstrated Performance 9-8
    Cost of Treatment 9-10
    Overall Status of Biological Treatment 9-20
10. Incineration Processes 10-1
    Overview 10-1
    Process Description 10-20
    Hazardous Waste Incinerator Performance 10-36
    Costs of Hazardous Waste Incineration 10-55
    Status of Development 10-68
11. Emerging Thermal Treatment Technologies 11-1
    Circulating Bed Combustion 11-2
    Molten Glass Incineration 11-11
    Molten Salt Destruction 11-20
    Pyrolysis Processes 11-28
    In Situ Vitrification 11-44
12. Use as a Fuel 12-1
    Process Descriptions 12-6
    Demonstrated Performance 12-13
    Cost of Treatment 12-28
    Status of Development 12-31
13. Land Disposal of Residuals 13-1
    Solidification/Chemical Fixation 13-4
    Macroencapsulation 13-7
14. Considerations for System Selection 14-1
    General Approach 14-3
    Assessment of Alternatives 14-4

Appendices

A Properties of Organic Solvents A-1
B Solvent Distillation Equipment B-1

FIGURES

Number		Page
4.1.1	Solvent wastes recycled by commercial reprocessors in Illinois	4-5
6.1	Process train for treating aqueous/organic leachate	6-2
6.2	Process train for treating waste solvent	6-4
6.3	Alternatives for incinerating contaminated solid wastes	6-6
7.1.1	Basic schematic for batch and continuous fractionation systems	7-5
7.1.2	McCabe-Thiele diagram for distillation	7-6
7.1.3	Reclamation of cold cleaning solvents via small batch stills (15 gpd)	7-38
7.1.4	Reclamation of cold cleaning solvents via medium batch stills (55 gpd)	7-39
7.1.5	Reclmation of cold cleaning solvents via a large continuous still (250 gpd)	7-40
7.1.6	Reclamation of vapor degreasing solvents (chlorinated hydrocarbons, $4.50/gallon)	7-41
7.1.7	Reclamation of waste paint thinner ($2.00/gallon)	7-43
7.1.8	Reclamation of waste paint thinner ($4.50/gallon)	7-44
7.2.1	Cross section of agitated thin film evaporator	7-49
7.2.2	Treatment train using an agitated thin film evaporator	7-52
7.2.3	Selection of Luwa evaporators based on waste viscosity	7-54
7.2.4	Required heat transfer surface area for distilling low boiling organics and concentrating aqueous solutions	7-56

FIGURES (continued)

Number Page

7.2.5 Required heat transfer surface area for dehydrating heavy pastes and stripping wastes to low residual organics 7-57

7.2.6 Heat transfer and evaporation rates in Luwa thin film evaporators 7-58

7.2.7 Threshold costs for onsite ATFE versus feed solids concentration 7-80

7.2.8 Threshold cost vs feed solids concentration for solvent recovery using ATFE 7-81

7.3.1 Typical steam stripping process 7-89

7.4.1 Air stripping towers 7-137

7.4.2 Air stripping schematic 7-139

7.5.1 Schematic of extraction process 7-154

7.6.1 Carbon adsorption flow diagram 7-192

7.6.2 Carbon Bed Configurations 7-198

7.6.3 Schematic of biological/carbon adsorption treatment train . . . 7-203

7.6.4 Schematic of carbon adsorption/biological treatment train . . . 7-205

7.6.5 Schematic of biophysical treatment train 7-207

7.6.6 Schematic of stripping/carbon adsorption treatment train . . . 7-208

7.7.1 Phenol removal and recovery system - solvent regenration of Amberlite adsorbent 7-230

7.7.2 Performance of resin adsorption bed 7-241

8.1.1 Wet air oxidation general flow diagram 8-3

8.1.2 4.5 MGD wastewater treatment facility 8-22

8.1.3 Installed plant costs versus capacity 8-23

8.1.4 Unit operating costs versus unit flow rate 8-25

8.2.1 Temperature-density diagram 8-33

FIGURES (continued)

Number | Page

7.2.5 Required heat transfer surface area for dehydrating heavy pastes and stripping wastes to low residual organics 7-57

7.2.6 Heat transfer and evaporation rates in Luwa thin film evaporators 7-58

7.2.7 Threshold costs for onsite ATFE versus feed solids concentration 7-80

7.2.8 Threshold cost vs feed solids concentration for solvent recovery using ATFE 7-81

7.3.1 Typical steam stripping process 7-89

7.4.1 Air stripping towers 7-137

7.4.2 Air stripping schematic 7-139

7.5.1 Schematic of extraction process 7-154

7.6.1 Carbon adsorption flow diagram 7-192

7.6.2 Carbon Bed Configurations 7-198

7.6.3 Schematic of biological/carbon adsorption treatment train . . . 7-203

7.6.4 Schematic of carbon adsorption/biological treatment train . . . 7-205

7.6.5 Schematic of biophysical treatment train 7-207

7.6.6 Schematic of stripping/carbon adsorption treatment train . . . 7-208

7.7.1 Phenol removal and recovery system - solvent regenration of Amberlite adsorbent 7-230

7.7.2 Performance of resin adsorption bed 7-241

8.1.1 Wet air oxidation general flow diagram 8-3

8.1.2 4.5 MGD wastewater treatment facility 8-22

8.1.3 Installed plant costs versus capacity 8-23

8.1.4 Unit operating costs versus unit flow rate 8-25

8.2.1 Temperature-density diagram 8-33

FIGURES (continued)

Number		Page
8.2.2	Properties of water at 250 atm	8-35
8.2.3	Schematic flow sheet of MODAR process	8-37
8.3.1	Schematic of top view of ULTROX pilot plant by General Electric (Ozone sparging system omitted)	8-51
8.4.1	Example process flowsheet - oxidation	8-66
8.4.2	Effect of H_2O_2 alone, UV alone, and H_2O_2 plus UV on decomposition of trichloroethylene (TCE) at 20°C, pH 6.8	8-70
8.4.3	Rates of reaction of halogenated aliphatics at 20°C and 30°C .	8-71
8.5.1	Schematic diagram of the Hoescht AG chlorolysis process	8-79
8.6.1	Soil cleaning process schematic	8-88
8.6.2	Probable reaction mechanism	8-90
9.1	Flowsheet and plot of oxygen demand and oxygen supply versus tank length for (a) conventional, (b) complete-mix, and (c) step-aeration activated-sludge processes	9-2
9.2	Estimated annual operating and materials costs as a function of wastewater treatment facility capacity	9-18
9.3	Estimated annual man-hours needed for wastewater treatment facility operation	9-19
10.1	Pretreatment option logical decision flow chart	10-19
10.2	Flow sheet of an incineration plant for hazardous wastes . . .	10-23
10.3	Rotary kiln incinerator with liquid injection capability . . .	10-29
10.4	Cross-section of a fluidized-bed furnace	10-33
10.5	Purchase cost of liquid injection system (May 1982)	10-62
10.6	Purchase cost of rotary kiln system (May 1982)	10-62
10.7	Purchase cost of hearth incinerators (mid 1982)	10-63
10.8	Purchase cost of waste heat boilers (July 1982)	10-63

FIGURES (continued)

Number Page

10.9 Purchase cost of scrubbing systems receiving 500 to 550°F gas (July 1982) 10-64

10.10 Purchasse costs for typical hazardous waste incinerator scrubbing systems receiving 1800 to 2200°F gas (July 1982). . 10-64

11.1.1 CBC incineration pilot plant located at GA Technologies 11-3

11.1.2 Chemical reactions that occur in CBC combustion chamber 11-5

11.2.1 Dirt purifier and hazardous waste incinerator 11-16

11.3.1 Molten salt combustion system 11-21

11.4.1 Continuous pyrolizer 11-29

11.4.2 Pyroplasma process flow diagram 11-34

11.4.3 Advanced electric reactor [Huber] 11-38

11.4.4 High temperature fluid wall process configuration for the destruction of carbon tetrachloride 11-40

11.5.1 Operating sequence of in situ vitrification 11-45

11.5.2 Off-gas containment and electrode support hood 11-46

11.5.3 Cost of in situ vitrfication for TRU wastes as functions of electrical rates and soil moisture [Fitzpatrick, 1984] . . 11-48

14.1 Solvent waste management options 14-2

14.2 Simplified decision chart for aqueous and mixed aqueous/ organic solvent waste stream treatment 14-9

14.3 Simplified decision chart for organic liquid solvent waste stream treatment 14-10

14.4 Approximate ranges of applicability of VOC removal techniques as a function of organic concentration in liquid waste streams 14-13

TABLES

Number		Page
2.1	Scheduling for Promulgation of Regulations Banning Land Disposal of Specified Hazardous Wastes	2-2
2.2	Performance Achieved by Treatment Technologies (mg/liter) . .	2-6
3.1.1	Consumption of Major Solvents (10^6 lbs/year)	3-2
3.1.2	Priority Solvent Industrial End Uses	3-4
3.1.3	Top 20 Industries Generating Solvent Wastes	3-5
3.1.4	Hazardous Solvent Waste Generation in the Paint and Coatings Manufacturing and Factory Applied Coatings Industry	3-7
3.1.5	Waste Solvent Generation by Type of Degreasing Operation . . .	3-9
3.2.1	Summary of Waste Generation and Management	3-23
3.2.2	Physical Form of Waste Ignitables and Solvents Managed at TSD Facilities (gpy)	3-26
3.2.3	Relative Rankings of Solvent Waste Constituents	3-28
3.2.4	Numbers of Small Quantity Generators and Waste Quantity by Waste Stream	3-31
3.3.1	Characteristics of RCRA Solvent Wastes by Waste Management Practice	3-32
3.3.2	Waste Recycling Reported in the Revised National Survey . . .	3-34
3.3.3	Relative Ranking by Degree of Recycling	3-36
3.3.4	Distribution of Offsite Recycled Waste Solvents by Previous Use (%)	3-37
3.3.5	Characteristics of Waste Solvents Recovered Offsite	3-38

TABLES (continued)

Number | | Page
3.3.6 Onsite Recycling Practices for Solvent and Ignitable Wastes . 3-40
3.3.7 Recovery Practices for RCRA Hazardous Wastes by Residual Category 3-41
3.3.8 Treatment of Solvent and Ignitable Wastes by Incineration . . 3-42
3.3.9 Physical Forms of Incinerated Solvents and Ignitables 3-44
3.3.10 Priority Solvents Incinerated in 1981 3-45
3.3.11 Most Frequently Practiced Treatment Techniques in Tanks for Ignitable Wastes 3-46
3.3.12 Quantities of Solvent Waste Streams Currently Managed by Land Disposal 3-48
4.1.1 Summary of Comercial Solvent Recycling Surveys 4-3
4.1.2 Cost for Solvent Recovery at Commercial Facilities 4-7
4.1.3 Waste Solvent Transportation Costs 4-8
4.2.1 Solvent Waste Quantity Requiring Alternative Treatment (MGY) . 4-9
4.2.2 Annual Treatment and Recovery Capacity Demand and Availability (million gallons/year) 4-11
5.1 Summary of Waste Reduction Cases 5-6
5.2 Summary of Documented Solvent Recycling Practices 5-13
5.3 Summary of Solvents Recycled via Two Waste Exchanges 5-29
5.4 Examples of Waste Reduction Techniques/Accomplishments (All Programs are Onsite) 5-32
5.5 Cost vs Savings for Waste Reduction Programs Carried Out by IBM Corporation at Various Locations 5-36
7.1.1 Boiling Points and Autoignition Points of Risk Solvents . . . 7-9
7.1.2 Azeotrope Formation of Compounds with Water 7-12
7.1.3 Sample Data on Azeotrope Formation 7-13
7.1.4 Relative Performance Ratings of Trays and Packings 7-18

TABLES (continued)

Number Page

7.1.5 Selection Guide for Tower Internals 7-18

7.1.6 Small Still Performance Evaluation 7-20

7.1.7 Summary: GCA/OSW Case Study 7-23

7.1.8 Methyl Chloroform/Freon Batch Distillation System Operating Information 7-24

7.1.9 Distillation Column Results 7-24

7.1.10 Projected Economic Benefits 7-27

7.1.11 Unit Costs 7-29

7.1.12 Estimated Cost of Recovery of Freon/Methyl Chloroform 7-30

7.1.13 Capital Costs for Onsite Solvent Recovery Systems (1982 Dollars) 7-33

7.1.14 Threshold Costs ($ per Gallon) for Onsite Recovery Systems for Varying Solids Contents and Percent Net Discounted Cash Flows (DCF) 7-34

7.1.15 Commercially Available Solvent Stills 7-45

7.2.1 Keys to Selecting Kontro Thin Film Evaporators 7-53

7.2.2 Typical Agitated Thin Film Evaporator Design Characteristics . 7-60

7.2.3 Process Data for Luwa Thin Film Evaporator Runs 7-62

7.2.4 Percent by Weight of Principal Organic Components 7-63

7.2.5 Plant A: Thin Film Evaporator Waste Compositions and Headspace Analysis 7-67

7.2.6 Analysis of Liquid Samples, Thin Film Evaporator, Plant B . . 7-69

7.2.7 Analysis of Product Samples, Thin Film Evaporator, Plant B . . 7-70

7.2.8 Analysis of Liquid Samples, Thin Film Evaporator, Plant C . . 7-71

7.2.9 Hourly Costs of Luwa Thin Film Evaporator 7-73

7.2.10 Processing Costs During Three Test Runs of the Luwa Thin Film Evaporator 7-75

TABLES (continued)

Number Page

7.2.11 1984 Plant A Capital and Operating Cost 7-76

7.2.12 Capital Cost Recovery Components for Onsite ATFE Recovery Systems 7-77

7.2.13 Threshold Costs for Onsite ATFE Recovery Systems for Varying Solids Contents and Percent Net Discounted Cash Flow (DCF) 7-78

7.2.14 Threshold Costs for Onsite Systems Versus Changes in Capacity Factor (Recovered Solvent) 7-82

7.3.1 Process Data for the Steam Distillation Unit 7-99

7.3.2 Percent by Weight of 1,1,1-Trichloroethane in the Waste Streams During Operation of the Steam Distillation Unit . . 7-100

7.3.3 Metal Analyses for the Steam Distillation Unit 7-101

7.3.4 Plant D: Characterization of Wastes 7-104

7.3.5 Plant "D" Batch Steam Stripper" Process Data 7-105

7.3.6 Industrial Steam Stripper Survey 7-108

7.3.7 Full-Scale Industrial Stipper Performance Summary 7-110

7.3.8 Processing Data for Bench-Scale Stream Stripping of Stream 221 7-113

7.3.9 Summary of Removal Efficiency Data for Stream 221A 7-114

7.3.10 Summary of Processing Data for Bench-Scale Steam Stripping of Ethylene Dichloride 7-116

7.3.11 Test Conditions and TOC Removals for Bench-Scale Steam Stripping With/Without Activated Carbon 7-118

7.3.12 Results of Bench-Scale Steam Stripping Runs Performed With/Without Lime Pretreatment 7-119

7.3.13 Test Results From Carbon Adsorption of Off-Gas From Steam Stripping - Run 6 7-121

7.3.14 Steam Stripping Costs for Wastewater Streams Containing Contaminants of Varying Henry's Law Constant 7-125

TABLES (continued)

Number | Page

7.3.15 Cost Components for Onsite Steam Stripping Solvent Recovery: (Example Case with 30% Solvent Content and Bottoms Used as Fuel) 7-127

7.3.16 Steam Stripping Cost Estimates as a Function of Throughput, Solvent Content and Disposal Method 7-129

7.4.1 Compounds of Interest with Henry's Law Constant Greater Than 1 x 10^{-3} atm-m^3/mol 7-140

7.4.2 Results of Pilot-Scale Air Stripping Study 7-146

7.4.3 Results of Bench-Scale Air Stripping Study 7-148

7.4.4 Results of Pilot-Scale Air Stripping Treatability Study . . 7-149

7.5.1 K_V Values for Aqueous/Solvent Systems 7-159

7.5.2 Expermimentally Measured Equilibrium Distribution Coefficients for Extraction From Water Into Undecane, (295-300 K) and 1-Octanol 7-161

7.5.3 Measured Values of K_D for Extraction of Acrolein From Water Into Various Solvents 7-162

7.5.4 Measured Equilibrium Distribution Coefficients (K_D) at 30°C for Extraction of Nitrobenzene From Water Into Various Solvents 7-164

7.5.5 Variable Measured in Spray Column Extractor Study 7-167

7.5.6 Results of Spray Column Extractor Runs 7-168

7.5.7 Results of RDC Extractor Runs 7-170

7.5.8 Conditions and Results for Mini-Plant Extraction Run 7-171

7.5.9 Results of Solvent Extraction Studies 7-173

7.5.10 Estimated Costs for a Liquid-Liquid Extraction System 7-174

7.5.11 Preliminary Extraction for Nitrobenzene Extraction Using Di-Isobutyl Ketone (DIBK) 7-176

7.5.12 Breakdown of Operating Costs for Extraction of Acrolein . . . 7-177

TABLES (continued)

Number Page

7.5.13 Estimation of Operating Cost: Extraction of Acrolein by MIBK 7-178

7.5.14 Advantages and Disadvantages of Extraction Types 7-180

7.6.1 Waste Characteritics That Affect Adsorption by Activated Carbon 7-186

7.6.2 Influence of Substituent Groups on Adsorbability 7-187

7.6.3 Carbon Adsorption Isotherm Data 7-189

7.6.4 Adsorption of Solvents and Other Organics by Activated Carbon 7-190

7.6.5 Properties of Several Commercially Available Carbons 7-196

7.6.6 Typical Properties of Powdered Activated Carbon (Petroleum Base) 7-197

7.6.7 Data Reported From Bench-Scale and Pilt-Scale GAC Systems . . 7-211

7.6.8 Data Reported From Full-Scale GAC Systems 7-212

7.6.9 Data Reported from Full-Scale PAC System 7-213

7.6.10 Direct Costs for Carbon Adsorption 7-215

7.6.11 Indirect Costs for Carbon Adsorption 7-216

7.6.12 Carbon Adsorption Costs 7-218

7.6.13 Removal Ratings for Organic Compounds 7-220

7.7.1 Physical Properties of Adsorbents 7-225

7.7.2 Typical Physical Properties of Ambersorb XE-340 7-226

7.7.3 Chemical Compounds Treated by Resin Adsorption 7-233

7.7.4 Adsorption of Solvents by Ambersorb XE-340 7-236

7.7.5 Removal of Chlorinated Solvents by Ambersorb XE-340 7-238

7.7.6 Pilot Plant Adsorption Summary 7-239

TABLES (continued)

Number Page

7.7.7 Cost of Adsorbents 7-242

7.7.8 Design Criteria--Trihalomethane Removal 7-243

7.7.9 Cost Comparison--GAC vs. Resin 7-244

8.1.1 One Hour Wet Oxidation 8-11

8.1.2 Products Identified From One Hour Oxidations at 320°C 8-11

8.1.3 Bench-Scale Wet Air Oxidation of Pure Compounds 8-12

8.1.4 Bench-Scale Wet Air Oxidation of Organics in Wastewaters . . . 8-14

8.1.5 Bench-Scale Wet Air Oxidation of Wastewaters 8-16

8.1.6 Pilot-Scale Wet Air Oxidation of Organic Compounds in Industrial Wastewater 8-18

8.1.7 Priority Pollutant Removals Using a PACT^{TM}/Wet Air Regeneration System for Domestic and Organic Chemicals Wastewater 8-21

8.1.8 WAO Costs Versus Flow 8-24

8.2.1 Dielectric Constants of Some Common Solvents 8-32

8.2.2 MODAR Treatment Costs for Organic Contaminated Aqueous Wastes 8-43

8.3.1 Relative Oxidation Power of Oxidizing Species 8-48

8.3.2 Design Data for a 40,000 gpd (151,400 L/day) ULTROX Plant . . 8-53

8.3.3 Ozonation Treatment of Solvents and Ignitables 8-55

8.3.4 Equipment Plus Operating and Maintenance Costs: 40,000 gpd UV/Ozone Plant 8-58

8.4.1 Relative Oxidation Power of Oxidizing Species 8-64

8.5.1 Typical Chlorinolysis Reactions 8-76

8.5.2 Operating Characteristics of Chloronolysis Processes 8-77

TABLES (continued)

Number | Page

8.5.3 Annual Operating Cost for Processing 25,000 Metric Tons/Year of a Mixed Vinyl Chloride Monomer and Solvent Waste at a Chlorolysis Plant 8-83

8.6.1 Dechlorination Processes 8-89

9.1 Typical Operating Parameters for Biological Treatment Processes 9-9

9.2 Removal Data for Biological Processes 9-11

9.3 Average Performance of Full-Scale Biological Treatment Facilities for Solvents of Concern (mg/L) 9-16

9.4 Estimated Capital Cost for Wastewater Treatment Units 9-19

10.1 Solvent Hazardous Waste Heats of Combustion 10-11

10.2 Characteristic Parameters for Several Solvent Hazardous Wastes 10-13

10.3 Waste Characteristic Data for Several Solvent Hazardous Waste Streams 10-15

10.4 Operating Parameters of Hazardous Waste Liquid Injection Incinerators 10-26

10.5 Operating Parameters for Rotary Kilns 10-31

10.6 Operating Parameters for Fluidized-Bed Incinerators 10-35

10.7 Solvent Constituents Present in Incinerated Waste Streams . . 10-37

10.8 Incineration Facilities Tested 10-38

10.9 Summary of Results of Incinerator Test Programs 10-41

10.10 PICs Found in Stack Effluents 10-45

10.11 Residuals Analysis at Four Full-Scale Incinerators 10-46

10.12 Performance Test Synopsis 10-48

10.13 Performance Test Synopsis 10-50

10.14 Performance Test Synopsis 10-52

TABLES (continued)

Number		Page
10.15	Fluidized-Bed Incinerator Performance Test Results	10-54
10.16	Survey of Hazardous Waste Incinerators - Costs of Incineration and Cost Impacting Factors	10-58
10.17	Elements of Capital Cost for Incineration Systems	10-60
10.18	Summary of Cost Data Compiled by MITRE Corporation, 1981 . . .	10-66
10.19	Number of Hazardous Waste Incinerators in Service in the U.S.A.	10-69
10.20	Summary of Incineration Technologies	10-81
11.1.1	Capacities of CBC Systems	11-7
11.1.2	Summary of Bag Sample Results	11-9
11.1.3	Test Results on Hazardous Wastes Circulating Bed Incinerator Pilot Plant	11-10
11.1.4	Circulating Bed Combustion Units	11-12
11.1.5	Circulating Bed Incinerator vs. Conventional Incinerators . .	11-14
11.3.1	PCB Combustion Tests in Sodium-Potassium-Chloride-Carbonate Melts [Edwards, 1983].	11-25
11.3.2	Summary of Pilot-Scale Results	11-26
11.4.1	Carbon Tetrachloride Test Results	11-36
11.4.2	Summary of Operating Parameters and Results for Huber AER Research/Trial Burns	11-43
12.1	Thermal Technologies Considered Appropriate for Burning Hazardous Waste as Fuel	12-2
12.2	Representative Heating Values of Virgin and Spent Solvents . .	12-4
12.3	Operating Specifications: Systech Cement Kiln Process	12-11
12.4	Operating Specifications of Commercial Aggregate Kilns Burning Wastes	12-12
12.5	Boiler Summary	12-15

TABLES (continued)

Number Page

12.6 Summary of Test Average DREs for Volatile POHC 12-18

12.7 Composition of Typical Waste Feed - Site G 12-20

12.8 Summary of POHC DREs, Percent -- Site G 12-21

12.9 Results of Engineering-Science Industrial Boiler Test Program 12-23

12.10 Calculated Destruction and Removal Efficiencies (Percent) . . 12-25

13.1 Compatibility of Selected Waste Categories with Different Waste Solidification/Stabilization Techniques 13-3

13.2 Present and Projected Economic Considerations for Waste Stabilization/Solidification Systems 13-4

13.3 Summary of Test Results on Toxic Organics 13-7

13.4 Encapsulated Waste Evaluated at the U.S. Army Waterways Experiment Station 13-9

13.5 Estimated Costs of Encapsulation 13-9

14.1 Guideline Considerations for the Investigation of Waste Treatment Technologies 14-6

14.2 Treatment Processes Potentially Applicable to Solvent Wastes 14-11

14.3 List of Hazardous Constituents and Treatment Options 14-14

14.4 Summary of Solvent Treatment Processes 14-18

14.5 Major Cost Centers for Waste Management Alternatives 14-23

BACKGROUND

Solvents are low molecular weight organic compounds that are widely used by all segments of American society. As a result of their widespread usage and their mobility within the environment, their presence is frequently detected in all media, including ground water. To combat the potential negative effects of solvent contamination, the 1984 amendments to the Resource Conservation and Recovery Act (RCRA) directed EPA to ban certain solvent wastes from land disposal to the extent required to protect human health and the environment. The ban is effective 8 November 1986, two years after the enactment of the amendments.

EPA has taken steps to meet this deadline by evaluating the availability and technological capability of land disposal alternatives. As a result of this evaluation, a 2-year national variance was proposed for wastewaters, solvent contaminated soils, and inorganic sludges and solids containing less than 10,000 ppm of organic constituents. The variance was based on a determination by EPA that the available capacity of alternative treatment technologies capable of achieving high destruction or removal efficiencies (i.e., low ppm range) for these wastes will be insufficient to accommodate the quantities managed in land disposal units.

The categories of wastes subject to the 8 November 1986 land disposal restrictions are identified in the 14 January 1986 Federal Register[1]. They include organic wastes characterized as RCRA waste codes F001 through F005 and commercial chemical products, manufacturing intermediates and spill residues containing solvents identified in these codes (i.e., priority solvents of concern). Land disposal restrictions for other RCRA wastes will be developed and implemented at later dates.

SCOPE

This summary of the Solvents Technical Resource Document provides information that can be used by environmental regulatory agencies and others as a source of technical information describing waste management options for solvents and other wastes containing low molecular weight organic compounds. These options include waste minimization (i.e., source reduction, reuse, recycling), treatment and disposal of waste streams. Although emphasis is placed on the collection and interpretation of performance data for proven technologies, the full range of waste minimization processes and treatment/recovery technologies that can be used to manage solvent wastes is discussed (see Table 1).

In general, treatment process selection will be limited to wastes possessing specific chemical, physical and flow characteristics. Applicable technologies for wastes with varying ranges in initial solvent concentration are provided in Figure 1. A summary of overall performance, applicable waste streams, residuals generation and status of development for the primary solvent waste treatment processes is provided in Table 2.

Determination of the overall applicability of these technologies for treating spent solvents requires an understanding of the nature of solvent wastes and current waste management practices. Thus, the range and variability in data requirements include solvent waste physical, chemical, and flow (i.e., rate, periodicity) characteristics which, in turn, necessitates an understanding of solvent waste industrial origins. An analysis of current waste management practices serves to identify available methods which have proven to be both technologically and economically capable of treating solvent wastes. To a significant extent, waste management alternatives which will permit industry to meet EPA disposal requirements have already been implemented. This occured in response to increased regulatory requirements and the improved economic viability of solvent waste minimization and treatment options. The latter resulted from increased disposal costs, liability, and technological developments.

Solvent waste generation, characteristics and management practices are briefly summarized below. This is followed by a discussion of potential waste management methods, including source reduction and recycling, which are applicable to solvent wastes (see Table 1). Emphasis is placed on identifying treatment process design and operating factors and waste characteristics which affect treatment/recovery of solvent wastes. This discussion concludes with a summary of technical and economic factors which should be considered in the selection of an optimal waste management system.

TABLE 1. WASTE MANAGEMENT ALTERNATIVES TO LAND DISPOSAL

Waste management objective	Applicable waste type(s)	Potential waste management alternative			
Waste Minimization					
Source Reduction	All	Raw material substitution Product reformulation	Process redesign Waste segregation		
Recycling	All	Reclamation	Reuse (e.g., as a fuel or process solvent)		
Pretreatment					
	Liquid with solids	Screening Floatation	Sedimentation Settling	Filtration Centrifugation	Distillation
	Liquid - Two Phase	Decanting Distillation	Floatation	Centrifugation	Extraction
	Sludge	Vacuum filtration	Filter press	Centrifugation	Other dewatering
	Bulky Solids	Shredders	Hammermills	Crushers	
	Low Btu/High Viscosity	Blending			
Treatment					
Physical	Liquid	Distillation Steam stripping	Evaporation Air stripping	Fractionation Carbon adsorption	Extraction Resin adsorption
Chemical	Liquid	Wet air oxidation Other chemical oxidations	Supercritical water oxidation	Chlorinolysis	Ozonation Dechlorination
Biological	Liquid	Activated sludge	Aerated lagoon	Trickling filter	
Incineration	All	Liquid injection	Rotary kiln	Fluidized-bed	Starved air
Other Thermal	All	Pyrolysis processes Plasma systems	Molten glass Electric reactor	Circulating fluid bed Molten salt	
Post Treatment					
	Organic Liquid	Decanting	Dehydrating	Fractionation	Thermal destruction
	Solid/Sludge	Solidification	Encapsulation	Thermal destruction	
	Aqueous Liquid	Carbon adsorption Ozonation	Resin adsorption Other oxidations	Air stripping	Biological treatment

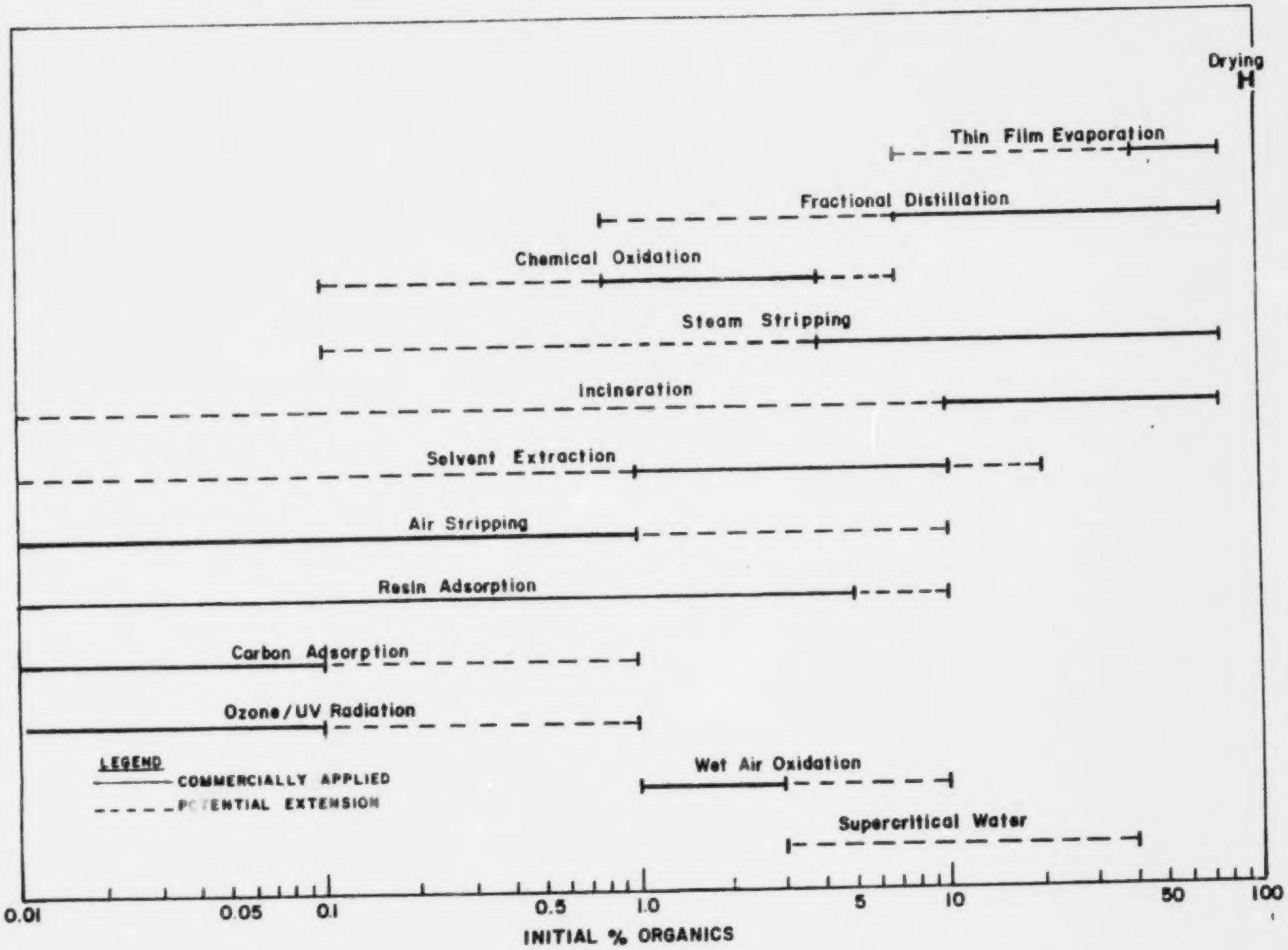

Figure 1. Approximate ranges of applicability of treatment techniques as a function of organic concentration in liquid waste streams.

Source: References 1 and 11.

TABLE 2. SUMMARY OF SOLVENT TREATMENT PROCESSES

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Incineration				
Liquid injection incineration	All pumpable liquids provided wastes can be blended to Btu level of 8500 Btu/lb. Some solids removal may be necessary to avoid plugging nozzles.	Estimated that over 219 units are in use. Most widely used incineration technology.	Excellent destruction efficiency (>99.99%). Blending can avoid problems associated with residuals, e.g., HCl.	TSP, possibly some PICs, and HCl if halogenated organics are fired. Only minor ash if solids removed in pretreatment processes.
Rotary kiln incineration	All wastes provided Btu level is maintained.	Over 40 units in service; most versatile for waste destruction.	Excellent destruction efficiency (>99.99%).	Requires APCDs. Residuals should be acceptable if charged properly.
Fluidized bed incineration	Liquids or nonbulky solids.	Nine units reportedly in operation-circulating bed units under development.	Excellent destruction efficiency (>99.99%).	As above.
Fixed/multiple hearths	Can handle a wide variety of wastes.	Approximately 70 units in use. Old technology for municipal waste combustion.	Performance may be marginal for hazardous wastes, particularly halogenated wastes.	As above.
Use As A Fuel				
Industrial kilns	Generally all wastes, but Btu level, chlorine content, and other impurity content may require blending to control charge characteristics and product quality.	Only a few units now burning hazardous waste.	Usually excellent destruction efficiency (>99.99%) because of long residence times and high temperatures.	Requires APCDs. Residuals should be acceptable.
High temperature industrial boilers	All pumpable fluids, but should blend halogenated organics. Solids removal particularly important to ensure stable burner operation.	Several units in use.	Most units tested have demonstrated high DRE (>99.99%).	Wastes must be blended to meet emission standards for TSP and HCl unless boilers equipped with APCDs.

(continued)

TABLE 2 (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Other Thermal Technologies				
Circulating bed combustor	Liquids or nonbulky solids.	Only one U.S. manufacturer. No units treating hazardous waste.	Manufacturer reports high efficiencies (99.99%).	Bed material additives can reduce HCl emissions. Residuals should be acceptable.
Molten glass incineration	Almost all wastes, provided moisture and metal impurity levels are within limitations.	Technology developed for glass manufacturing Not available yet as a hazardous waste unit.	No performance data available, but DREs should be high (99.99%).	Will need APC device for HCl and possibly PICs; solids retained (encapsulated) in molten glass.
Molten salt destruction	Not suitable for high (20%) ash content wastes.	Technology under development since 1969, but further development on hold.	Very high destruction efficiencies for organics (six nines for PCBs).	Needs some APC devices to collect material not retained in salt. Ash disposal may be a problem.
Furnace pyrolysis units	Most designs suitable for all wastes.	One pyrolysis unit RCRA permitted. Certain designs available commercially.	Very high destruction efficiencies possible (99.99%). Possibility of PIC formation.	TSP emissions lower than those from conventional combustion . Will need APC devices for HCl. Certain wastes may produce an unacceptable tarry residual.
Plasma arc pyrolysis	Present design suitable only for liquids.	Commercial design appears imminent, with future modifications planned for treatment of sludges and solids.	Efficiencies exceeded six nines in tests with solvents.	Requires APC devices for HCP and TSP, needs flare for H_2 and CO destruction.
Fluid wall advanced electric reactor	Suitable for all wastes if solids pretreated to ensure free flow.	Ready for commercial development. Test unit permitted under RCRA.	Efficiencies have exceeded six nines.	Requires APC devices for TSP and HCl; Chlorine removal may be required.
In situ vitrification	Technique for treating contaminated soils, could possibly be extended to slurries. Also use as solidification process.	Not commercial, further work planned.	No data available, but DREs of over six nines reported.	Off gas system needed to control emissions to air. Ash contained in vitrified soil.

(continued)

TABLE 2. (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Physical Treatment Methods				
Distillation	This is a process used to recover and separate solvents. Fractional distillation will require solids removal to avoid plugging columns.	Technology well developed and equipment available from many suppliers; widely practiced technology.	Separation depends upon reflux (99+ percent achievable). This is a recovery process.	Bottoms will usually contain levels of solvent in excess of 1,000 ppm; condensate may require further treatment.
Evaporation	Agitated thin film units can tolerate higher levels of solids and higher viscosities than other types of stills.	Technology is well developed and equipment is available from several suppliers; widely practices technology.	This is a solvent recovery process. Typical recovery of 60 to 70 percent.	Bottoms will contain appreciable solvent. Generally suitable for incineration.
Steam Stripping	A simple distillation process to remove volatile organics from aqueous solutions. Preferred for low concentrations and solvents with low solubilities.	Technology well developed and available.	Not generally considered a final treatment, but can achieve low residual solvent levels.	Aqueous treated stream will probably require polishing. Further concentration of overhead steam generally required.
Air Stripping	Generally used to treat low concentration aqueous streams.	Technology well developed and available.	Not generally considered a final treatment, but may be effective for highly volatile wastes.	Air emissions may require treatment.
Liquid-Liquid Extraction	Generally suitable only for liquids of low solid content.	Technology well developed for industrial processing.	Can achieve high efficiency separations for certain solvent/waste combinations.	Solvent solubility in aqueous phase should be monitored.
Carbon Adsorption	Suitable for low solid, low concentration aqueous waste streams.	Technology well developed; used as polishing treatment.	Can achieve low levels of residual solvent in effluent.	Adsorbate must be processed during regeneration. Spent carbon and wastewater may also need treatment.
Resin Adsorption	Suitable for low solid waste streams. Consider for recovery of valuable solvent.	Technology well developed in industry for special resin/solvent combinations. Applicability to waste streams not demonstrated.	Can achieve low levels of residual solvent in effluent.	Adsorbate must be processed during regeneration.

(continued)

TABLE 2. (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Chemical Treatment Processes				
Wet air oxidation	Suitable for aqueous liquids, also possible for slurries. Solvent concentrations up to 15%.	High temperature/ pressure technology, widely used as pretreatment for municipal sludges, only one manufacturer.	Pretreatment for biological treatment. Some compounds resist oxidation.	Some residues likely which need further treatment.
Supercritical water oxidation	For liquids and slurries containing optimal concentrations of about 10% solvent.	Supercritical conditions may impose demands on system reliability. Commercially available in 1986.	Supercritical conditions achieve high destruction efficiencies (>99.99%) for all constituents.	Residuals not likely to be a problem. Halogens can be neutralized in process.
Ozonation	Oxidation with ozone (possibly assisted by (UV) suitable for low solid, dilute aqueous solutions.	Now used as a polishing step for wastewaters.	Not likely to achieve residual solvent levels in the low ppm range for most wastes.	Residual contamination likely; will require additional processing of off gases.
Other chemical oxidation processes	Oxidizing agents may be highly reactive for specific constituents in aqueous solution.	Oxidation technology well developed for cyanides and other species (phenols), not yet established for general utility.	Not likely to achieve residual solvent levels in the low ppm range for most wastes.	Residual contamination likely; will require additional processing.
Chlorinolysis	Suitable for any liquid chlorinated wastes.	Process produces a product (e.g., carbon tetrachloride). Not likely to be available	Not available.	Air and wastewater emissions were estimated as not significant.
Dechlorination	Dry soils and solids.	Not fully developed.	Destruction efficiency of over 99% reported for dioxin.	Residual contamination seems likely.
Biological Treatment Methods				
	Aerobic technology suitable for dilute wastes although some constituents will be resistant.	Conventional treatments have been used for years.	May be used as final treatment for specific wastes, may be pretreatment for resistant species.	Residual contamination likely; will usually require additional processing.

SOLVENT WASTE GENERATION, CHARACTERISTICS AND MANAGEMENT PRACTICES

Of the more than 8 billion gallons of organic solvent compounds consumed annually, approximately 60 percent consists of priority solvents which may ultimately be affected by the upcoming land disposal restrictions. Of this, 64 percent are nonhalogenated solvents. These are widely used in the paint and allied products industry as ingredients and wash solvents and in general industry applications as cold cleaners. The remainder are halogenated compounds which are primarily used as vapor degreasers, cold cleaners, and dry cleaning solvents.

Hazardous solvent wastes are generated at a rate of 4 to 8 billion gallons annually, the majority of which are dilute, solvent contaminated aqueous wastes. However, the bulk of waste solvent constituents are found in non-aqueous streams; i.e., greater than 1 percent total organics. Of these, roughly 1.5 billion gallons are managed in RCRA treatment, storage, and disposal facilities with 60 percent being recycled.

Although there are some exceptions, nonaqueous solvent waste generation and recycling tend to parallel solvent consumption. This occurs because solvents are used in nonconsumptive applications and are recycled (onsite or offsite) to approximately the same extent. On average, low cost solvents typically result in larger volume waste streams (e.g., wash solvents) which provides comparable economic incentives (e.g., high disposal cost, economies of scale) to recover relative to more expensive solvents; e.g., chlorinated degreasing solvents. In addition, nonhalogenated waste solvents and treatment residuals find widespread use as fuel supplements relative to halogenated compounds.

Organic liquids comprise the vast majority of currently recycled waste solvents with aqueous, solid, and sludge wastes contributing little to total recycled quantity. Landfills are used as the primary management method for a disproportionately high fraction of solids, sludges, halogenated, and low volume solvent wastes. Conversely, large volume, liquid, and nonhalogenated solvents have a higher tendency to be treated via other methods; e.g., tanks and wastewater technologies.

Although over one-third of currently landfilled solvents wastes contain over 10 percent solvent, these wastes tend to be low volume streams which generators could not justify reusing or recycling. However, higher disposal costs, recent technological developments (e.g., low cost, high recovery package distillation systems), technology transfer, and increased availability of offsite management alternatives (e.g. solvent reclaimers, waste exchanges) have resulted in a corresponding increase in solvent recylcing.

This trend in recycling should be accelerated upon implementation of the land disposal restrictions since recycling and other forms of waste minimization will become the next lowest cost alternative for managing many solvent wastes. In the short term, use of evaporation technologies which yield high solvent recoveries will reduce overall solvent quantity requiring land disposal but probably result in the generation of more solvent solids and sludges (less than 10,000 ppm solvent). These wastes and aqueous streams will be subject to a two year extension of the land disposal ban as noted previously. In that period, implementation of waste minimization efforts should decrease net volume of solvent waste requiring disposal and create a shift in the distribution of these waste from aqueous to sludge/solid physical form.

EPA feels that alternative treatment capacity for solvent wastes will be available under the proposed disposal ban schedule. This determination was based on estimates of current waste quantities disposed, small quantity generator disposal requirements, projected residuals generated as a result of increased use of recovery technologies and available treatment capacity. Capacity shortfalls should not occur as a result of the conservative assumptions used in EPA's analysis regarding available treatment capacity. EPA assumed that only available offsite incineration and wastewater treatment would be available as land disposal alternatives due to lack of data on other options. Specifically, data gaps include available onsite capacity, impact of waste minimization, availability of emerging treatment processes capable of yielding high removal efficiencies, and uncertainties surrounding the future regulation of hazardous waste use as a fuel. EPA was not able to consider these in its analysis despite the fact that they will result in both lower demand and increased available treatment capacity.

WASTE MINIMIZATION

Waste minimization alternatives consist of two basic approaches, source reduction and recycling. Individual case studies of waste minimization programs have been extensively documented, which show net cost savings and rapid payback periods on equipment purchases for both large and small waste generators. For example, over a period of 3 years, IBM reported a waste reduction of 234 million pounds of solvent wastes at five plants which resulted in a net cost savings of 120 million dollars. Due to the site specific nature of these applications, it is difficult to estimate the national impact of future activities on overall waste generation. Waste minimization programs are likely to significantly decrease solvents currently land disposed. To date, these programs have been more commonly applied to solvent wastes relative to other hazardous wastes primarily as a result of favorable economics.

Source reduction represents a preventive approach to hazardous waste management which can be accomplished through raw material substitution, product reformulation, process modifications, or waste segregation. Recycling can either take the form of direct reuse in a process which tolerates lower solvent quality specifications or involves some form of reclamation prior to reuse. Considerations for both source reduction and recycling include impacts on product quality, process performance, and net cost savings relative to the use of virgin products and other waste management options.

Primary recycling methods currently in use include some form of distillation or evaporation, decanting, filtration, and less commonly, fractionation and steam stripping. Extraction and adsorption processes are less frequently used to recover RCRA solvent wastes. The majority of priority solvents are recycled as a reclaiment while ignitable wastes are primarily used as fuel supplements. Other recycling methods include direct reuse as a feedstock. Halogenated solvents are finding increased use as cement kiln and iron blast furnace fuel supplements with small amounts being used as an extender in the manufacture of concrete blocks and asphalt.

PRETREATMENT

The purpose of pretreatment is to remove restrictive waste characteristics to simplify or reduce costs of subsequent treatment. Most pretreatment methods involve physical separation of different phases or chemical species or modification of the waste physical form. Commonly applied pretreatment methods have been summarized in Table 1 for various waste types.

PHYSICAL TREATMENT PROCESSES

Physical treatment processes are the most commonly applied methods used to treat solvent wastes. Highly concentrated organics (i.e., greater than 10 percent solvent) are generally treated through some form of distillation/evaporation. Steam stripping is used for insoluble organic species and fractionation used for separating mixtures or recovering high purity products. Steam stripping can also be used, along with solvent extraction and resin adsorption, for aqueous wastes with organic solvent levels below 10 percent. Air stripping and carbon adsorption are only economically applied to wastes with solvent concentration at 1 percent or less.

Pretreatment requirements include varying degrees of solids, oil, grease, metals, and nonhazardous organic contaminant removal to prevent fouling of heat or mass transfer surfaces. Waste constituents which are generally most difficult to separate via physical mechanisms include those which are highly soluble (e.g., alcohols) and those which have low volatility relative to the bulk of the waste stream; e.g., nitrobenzene or cresol contaminated wastewater. Under favorable conditions, adsorption and stripping processes are capable of yielding residual products which can be discharged without requiring additional treatment.

Distillation/evaporation processes are the most widely applied technologies for recovering concentrated organic wastes. Separation efficiencies of well over 90 percent have been reported. However, removal is limited due to constraints imposed by vapor liquid equilibrium (e.g., azeotrope formation, low differential vapor pressure), restrictive waste characteristics (e.g., presence of contaminants that foul heat transfer or packing surfaces, low thermal decomposition and autoignition temperatures, high viscosity), and economics; e.g., high residence time, capital cost and operating temperature and low pressure requirements. With conventional equipment, bottoms must be kept in a pumpable state which often represents the most limiting factor in solvent recovery.

Fractionation is used for separating mixtures of volatile organics from waste streams containing minimal solids content. It is frequently applied as a post treatment purification step. The other extreme in high volume processing equipment is agitated thin film evaporators. These units can handle wastes with viscosities up to one million centipoises and have been economical in processing wastes with as little as 6 to 8 percent recoverable solvent. These units are widely applied by commercial solvent reclaimers due to their high potential recoveries and minimal pretreatement requirements. Removal efficiencies are maximized in these units as a result of their capability of processing high viscosity wastes in turbulent conditions. This minimizes the adverse effect of mass transfer resistance on volatilization rate and enables residual solvent levels to be reduced below 100 ppm under favorable conditions.

Recent technological innovations in distillation/evaporation equipment include development of semi-batch, low volume, package systems which permit processing to solid or sludge bottoms products. Use of these and other solids handling equipment (e.g., drum dryer, jacketed heating vessel with mechanical driver to maintain waste flow) result in maximum solvent recovery and minimum volume of waste requiring subsequent disposal. Alternatively, mixing distilling liquids with nonvolatile carrier fluids (e.g., waste oil) allows for higher recovery efficiency while maintaining pumpable bottoms. These techniques and equipment are currently applied primarily to halogenated solvent wastes to minimize disposal/blending costs but will find widespread use for all solvents when land disposal is no longer a viable management option.

Steam stripping is most effectively applied in aqueous solutions (less than 10 percent solvent) for the removal of volatile components (boiling point less than 150°C, Henry's law constant greater than 10^{-4} atm-m^3/mole) that are only slightly soluble in water (less than 1,000 ppm). It can also be used for stripping organic solutions when water forms low boiling azeotropes with the compounds to be removed and does not adversely affect overhead or bottoms quality. Steam stripping is widely applied to separate halogenated and certain aromatics from water, but is less effective for stripping miscible organics such as ketones or alcohols. Since there are no heat transfer surfaces and bottoms remain fluid, steam stripping can tolerate higher contaminant quantities relative to conventional distillation. Under ideal conditions, bottoms products may not require additional treatment.

In general, steam stripping is more cost effective than air stripping for waste with appreciable solvent content; i.e., greater than 1 percent. Air stripping has only found significant commercial application in treating solvent contaminated water supplies with concentrations of a few parts per million or less. The technology has demonstrated high removal efficiencies for volatile organics and, thus, may find increased use as a polishing treatment step; e.g., for compounds resistant to biodegradation or exhibiting low adsorption characteristics.

Liquid-liquid extraction is not a commonly used treatment method but it has potential for treating aqueous wastes which are not readily treated through more conventional methods. Extraction can be attractive in cases where the solutes are present at high enough concentrations to prohibit use of adsorption, are toxic to biological organisms, and when steam stripping is less effective as a result of low solute volatility or formation of azeotropes. Extraction is most cost effective when solutes are in the 1 to 10 percent concentration range. Costs can be high as a result of solvent regeneration requirements and post treatment costs associated with removal of residual solvent from the treated aqueous stream.

Carbon and resin adsorption can be used for treating dilute aqueous wastes to levels which permit discharge as a nonhazardous waste. Carbon adsorption is a widely applied technology for effluent polishing. It can be used to treat wastes with up to 5,000 ppm organics and 1,000 ppm inorganics. However, it is more typically used for wastes with less than 1,000 ppm organics due to high regeneration costs (thermal regeneration is typically required). Activated carbon is most effective in removing nonpolar, low solubility (less than 0.1 mg/L), high molecular weight (greater than 100) compounds. Pretreatment to remove oil and grease (less than 10 mg/L), suspended solids (10 to 70 mg/L depending on carbon treatment flow configuration) and nonhazardous organics (biological pretreatment) which compete for adsorption sites or clog macropores minimizes required regeneration frequency. Powdered activated carbon is frequently used in conjunction with biological treatment. The carbon acts as a buffer to minimize the adverse effects of high or variable concentrations of toxic compounds.

Resins are significantly more expensive than natural carbon base materials; however, they offer improved processing capabilities. Resins can be manufactured to have higher polarity and more controlled pore size distributions and are consequently capable of achieving higher removal efficiencies for certain compounds. They are more easily regenerated through extraction processes which extends their capability for treating wastes with higher initial solvent concentration (up to 5 percent). This is especially desirable if recovery of solvent is economically feasible.

Finally, adsorption and extraction processes are also used as a polishing step for dehydrating solvent streams such as decanted overhead products from distillation or steam stripping. Drying methods which are currently in use include caustic extraction and molecular sieve, calcium chloride and ionic resin adsorption.

CHEMICAL TREATMENT PROCESSES

Chemical treatment methods for solvent wastes include oxidation, chlorinolysis, and dechlorination processes. The most important of these processes is oxidation. Of particular interest is the supercritital water oxidation (SWO) process developed by MODAR, Inc. The first commercial SWO unit is now being designed to treat up to 30,000 gallons of aqueous waste per day with installation scheduled for late 1987. Although the characteristics of the aqueous waste have not been made public at this time, a solvent concentration of about 10 percent is reported to be thermally optimal for the process. On the basis of reported test data, the destruction and removal efficiency (DRE) is anticipated to be at the six nines level for all halogenated and nonhalogenated solvent constituents.

In addition to high DRE, another feature of the SWO process is its applicability to the treatment of halogenated organics. Hydrochloric acid formed as a result of oxidation of chlorinated compounds can be neutralized within the system by prior addition of caustic to the feed stream. The chloride salts formed (and other inorganic salts) are essentially insoluble in water at super critical conditions and are removed from the process stream by a separator which is an integral part of the SWO system design. Ultimately, the applicability of SWO to the treatment of solvent wastes in aqueous streams will depend on the economics of the process. The economics in turn, will depend upon the ability of the process equipment to withstand stringent supercritical temperature and pressure requirements which are in excess of 374°C and 218 atmospheres.

The wet air oxidation (WAO) process, which operates at subcritical and therefore less stringent temperature and pressure conditions (e.g., less than

320°C and 200 atmospheres), may also have some application for the treatment of solvent wastes in aqueous media. However, the DREs will not be as high as those achieved by the SWO process. This is particularly true for chlorinated aromatics such as chlorobenzene which are highly resistant to oxidation under WAO conditions. In addition, low molecular weight residuals which resist further degradation, such as acetic acid and formic acid, are commonly reported as byproducts of aqueous solvent wastes treated by the WAO process.

The WAO process is an established technology for the treatment of municipal sludges. Ithas also found application for the treatment of a limited number of specific waste streams, including acrylonitrile and coke oven gas scrubbing wastewaters. While the WAO process may also find utility for the treatment of other specific waste streams, it may prove to be most useful as a pretreatment for solvent waste streams which are too dilute to incinerate and yet too toxic to biotreat. Available data indicate that solvent streams that are resistant to biological treatment can generally be detoxified by the WAO process to allow subsequent effective biological degradation.

Other chemical oxidation processes that have been used for the degradation of solvent wastes operate at ambient or only moderately elevated conditions of temperature and pressure. Primary oxidation agents include ozone, hydrogen peroxide, and potassium permanganate. These oxidants have found application as polishing agents for dilute organic contaminated wastewater or as oxidants for specific organics (e.g., aldehydes and phenols) in industrial waste streams. However, their applicability to solvent waste streams appears to be limited. Process residuals are usually found which will often require additional treatment to produce an environmentally acceptable discharge stream. Furthur, the indiscriminate nature of the oxidation process limits its application to the treatment of hazardous aqueous water. Cost and, in some cases, the need for stringent process control measures, become prohibitive if organic slurries and slurries are to be treated.

There is some evidence to indicate that the efficiency and completeness of oxidation is enhanced by UV photolysis. However, the evidence is limited and the sensitivity of photolysis to the presence of impurities in the process stream is an issue of concern.

The chlorinolysis and dechlorination processes do not appear to have general application for the treatment of solvent wastes. Chlorinolysis is a pyrolysis process conducted in the presence of chlorine to produce low molecular weight chlorinated compounds (e.g., carbon tetrachloride) using chlorine bearing wastes from sources such as the pesticide industry. The process has not yet been utilized in the United States. It requires high levels of capital expenditure and is economically dependent upon the return available from the sale of the chlorinated hydrocarbon product. It is unlikely that the process will become available in the forseeable future.

The dechlorination processes examined are experimental processes that are being developed primarily for the treatment of highly toxic dioxin compounds. Although they are capable of achieving high solvent DREs, the alkali metal based reactants used in these processes are expensive and highly reactive. Other technologies appear to be more suitable.

BIOLOGICAL TREATMENT

Despite the almost universal use of cost effective, biological methods for the treatment of wastes, very little information could be found describing DREs for the constituents in solvent-bearing wastes. Data are available for aerobic systems showing discharge concentrations for many solvents that are below the ppm level. However, these data are based on influent levels that, while sufficient to demonstrate significant DREs, are not high enough to exhibit appreciable inhibitory biological effects. Some degree of pretreatment through technologies such as WAO, carbon adsorption, or solvent extraction will be required for many wastes containing high levels of organic compounds, particularly the more biotoxic halogenated compounds. As noted, addition of powdered activated carbon to activated sludge has proven effective in mitigating the inhibitory activity of solvent constituents to biological activity.

THERMAL DESTRUCTION TECHNOLOGIES

The thermal destruction of organic solvent wastes has been the subject of EPA research for several years. DREs in excess of the 99.99 percent requirement for incinerators have been well documented for most solvents of concern present in various types of waste. Documentation is particularly extensive for the halogenated compounds considered most difficult to thermally destroy. Incineration techniques that represent proven technology include liquid injection; fixed hearth, including those using starved-air designs rotary kilns, and fluidized-bed incineration. The incineration of many solvent wastes will require air pollution control devices to achieve the incinerator requirements of:

- At least 99 percent removal of hydrogen chloride from the exhaust gas if hydrogen chloride emissions are greater than 4 lb/hr; and
- Particulate emissions not exceeding 0.08 grains/dry standard cubic feet, corrected to 7 percent oxygen in the stack gas.

In 1981, prior to the promulgation of the 1982 incinerator standards, over half of the operating incinerators were not equipped with air pollution control systems for either particulates or acid gases. Although the present status of control device application at incinerators is now being assessed by EPA, it is possible to comply with the incinerator standards by restricting waste feed streams to those low ash, nonhalogenated wastes for which control measures will not be necessary.

Because of the broad applicability of thermal destruction to solvent wastes and the added demands for alternatives to land disposal resulting from the 1984 RCRA amendments, a number of emerging thermal technologies are in various stages of development. Several pyrolysis processes, molten glass and molten salt technologies, circulating bed combustion and the in situ vitrification processes are among the more prominent. Pyrolysis processes are particularly well advanced with two processes, a furnace design manufactured by the Midland-Ross Corporation and the Huber advanced electric reactor now operating under RCRA permit status. A third process, under development by Pyrolysis Systems, Inc. of Welland Ontario, is now undergoing intensive testing by EPA. All of the pyrolysis units should meet DRE requirements but will have to or already have incorporated control systems for particulates and acid gases.

The molten glass furnace is based on technology long established in the glass industry. Although no units are now operating commercially, two companies are actively pursuing development. DREs of 99.99^+ percent can be anticipated, although interest in this process has also focussed on its potential for containing solid and inorganic residues within a stable, nonleachable glass matrix. The destruction principle is similar in concept to that of the Molten Salt Destruction Technology. This latter technology, under development by Rockwell since 1969, has achieved greater than 99.9 percent DRE. However, solid residues must be freed from the salt matrix during regeneration and may require further treatment. Although three units (maximum capacity 2,000 lb/hour) have been built by Rockwell, no commercial units have been sold. At the present time no further development is planned by Rockwell.

The circulating bed combustor is an outgrowth of conventional fluidized bed combustion technology. By using high velocities and a circulating bed, potential problems associated with maintaining the critical flow velocity needed for bed stability are avoided. Turbulence is also increased, which should enhance DRE (already demonstrated to be in excess of 99.99 percent for solvents). Addition of limestone to the bed can effectively reduce hydrochloric acid emissions from halogenated solvent combustion. However, pollution control systems will be required to meet the incinerator standards for particulate emissions.

The in situ vitrification process is designed to treat contaminated soils rather than process waste streams. Now under development by Battelle Northwest, DREs in excess of 99.99 percent have been achieved in the laboratory for solvents. An added feature of this technology is the encapsulation of solid wastes in a vitrified matrix which is leach resistant and durable. Work, some of it supported by the Electric Power Research Institute, is continuing, with focus on PCB rather than solvent, contaminated soils.

USE AS A FUEL

Thermal destruction of solvents wastes in industrial boilers and other high temperature industrial processing equipment (e.g., cement, lime, and aggregate kilns) has been actively studied by EPA in recent years. Performance data indicate that most industrial boilers and processing units can meet the incinerator DRE standard of 99.99 percent for solvent constituents. No difficulties were encountered in meeting the 4 lb/hr emission standard for hydrogen chloride during the combustion of nonhalogenated solvent wastes. Also, no significant changes in particulate emissions were observed that could be attributed to the burning of waste fuels. The particulate emission standard of 0.08 grains per dry standard cubic feet at 7 percent oxygen can be met by a waste with an ash content of about 0.3 percent. The exact value will depend upon the Btu value of the fuel, its elemental composition, and other factors. Blending of many low ash content wastes with conventional fuel oils prior to combustion could avoid the need to install costly pollution control devices for many wastes.

LAND DISPOSAL OF RESIDUALS

Ash residues from thermal destruction processes, including burning of wastes in industrial boilers and process equipment, appear to be acceptable for land disposal. However, they and other treatment residuals may be required to undergo solidification or encapsulation prior to land disposal. Present understanding of the interaction of solvent containing wastes and residuals with various solidification materials is limited and long term interactions can only be inferred from short term behavior. Potential problems associated with the disposal of process residuals is a major factor in assessing alternatives to land disposal.

SELECTION OF OPTIMAL WASTE MANAGEMENT ALTERNATIVE

Waste management options have been summarized previously in Table 1. These include source reduction, recycling, use of a treatment system or some combination of these waste handling practices. Selection of the optimal management alternative will ultimately be a function of regulatory compliance, economics, and availability of onsite and offsite systems and equipment. Economic considerations include processing (including pretreatment and post-treatment) and disposal costs, value of recovered products, and potential adverse effects on product quality or process equipment resulting from waste minimization or reuse of recovered products. Additional consideration in system selection must be given to factors such as safety, public and employee acceptance, liability, and degree of uncertainty in cost estimates and ability to meet treatment objectives.

SECTION 1.0

INTRODUCTION

This Technical Resource Document provides information that can be used by environmental regulatory agencies and others as a source of technical information for waste management options for solvent wastes* and many other wastes containing low molecular weight organic compounds. These options include waste minimization, recycling, and treatment of waste streams. Emphasis has been placed on the collection and interpretation of performance data for proven technologies. These are:

- incineration
- use as a fuel
- distillation
- steam stripping
- biological treatment
- activated carbon adsorption

These, and other potentially viable technologies, are described in terms of their actual performance in removing constituents of concern, their associated process residuals and emissions, and those restrictive waste characteristics which impact the ability of a technology to effectively treat the wastes under consideration. Although emphasis is placed on performance data, cost and capacity data are provided to assist the user of this document in assessing the applicability of technologies to specific solvent wastes. References are cited throughout to identify additional sources of background information for the user.

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*Solvent wastes are those in RCRA Codes F001 through F005 plus those U and P type wastes containing the solvent constituents identified in the F001 through F005 Codes.

This document provides, in following sections, first a review of regulatory background (Section 2.0), and a review of the current hazardous waste management data base regarding sources of wastes and existing management practices (Sections 3.0 and 4.0). This is followed by information concerning waste minimization practices (Section 5.0) and an evaluation of the full range of treatment/recovery processes (Section 6.0 through 13.0). In order of their presentation, the latter include:

6.0 Pretreatment
7.0 Physical Treatment Processes
8.0 Chemical Treatment Processes
9.0 Biological Methods
10.0 Incineration Processes
11.0 Emerging Thermal Treatment Technologies
12.0 Use as a Fuel
13.0 Land Disposal of Residuals

These technologies are examined with emphasis placed on identifying process design and operating factors and waste characteristics which affect treatment/recovery of solvent wastes. Cost data are also presented to assist the user in evaluating and selecting options. Approaches to the selection of treatment/recovery options are reviewed in the final section of this document (Section 14.0). Pertinent properties of the compounds addressed in this document which impact treatment technology/waste interactions are provided in Appendix A.

SECTION 2.0

BACKGROUND

Section 3004 of the Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA), prohibits the continued placement of RCRA-regulated hazardous wastes in or on the land, including placement in landfills, land treatment areas, waste piles, and surface impoundments (with certain exceptions for surface impoundments used for the treatment of hazardous wastes). The amendments specify dates by which these prohibitions are to take effect for specific hazardous wastes. After the effective date of a prohibition, wastes may only be land disposed if: (1) they comply with treatment standards promulgated by the Agency that minimize short term and long term threats arising from land disposal or (2) the Agency has approved a site-specific petition demonstrating, to a reasonable degree of certainty, that there will be no migration from the disposal unit for as long as the waste remains hazardous. In addition, the statute authorizes the Agency to extend the effective dates of prohibitions for up to 2 years nationwide if it is determined that there is insufficient alternative treatment, recovery or disposal capacity.

2.1 SCHEDULE FOR LAND DISPOSAL PROHIBITION

The amendments call for the banning of the land disposal of solvents within 24 months of the 8 November 1984 enactment of the amendments. EPA must also determine whether to ban the land disposal of the "California List" and other listed wastes according to schedule shown in Table 2.1.

TABLE 2.1. SCHEDULING FOR PROMULGATION OF REGULATIONS BANNING LAND DISPOSAL OF SPECIFIED HAZARDOUS WASTES

Waste category	Effective date*
• Dioxin containing waste	11/8/86
• Solvent containing hazardous wastes numbered F001, F002, F)03, F004, F005	11/8/86
• California List	
-Liquid hazardous wastes, including free liquids associated with any solid or sludge containing:	
- Free or complex cyanides at $\geq$1,000 mg/L	7/8/87
- As $\geq$500 mg/L	
- Cd $\geq$100 mg/L	
- Cr^{+6} $\geq$500 mg/L	
- Pb $\geq$500 mg/L	
- Hg $\geq$20 mg/L	
- Ni $\geq$134 mg/L	
- Se $\geq$100 mg/L	
- Tl $\geq$130 mg/L	
-Liquid hazardous wastes with:	
- pH $\leq$2.0	7/8/87
- PCBs $\geq$50 ppm	
- Hazardous wastes containing halogenated organic compounds in total concentration $\geq$1,000 mg/kg	7/8/87
• Other listed hazardous wastes (§§261.31 and 32), for which a determination of land disposal prohibition must be made:	
- One-third of wastes	8/8/88
- Two-thirds of wastes	6/8/89
- All wastes	5/8/90
• Hazardous wastes identified on the basis of characteristics under Section 3001	5/8/90
• Hazardous wastes identified or listed after enactment	Within 6 months

*Not including underground injection.

2.2 TREATMENT STANDARDS FOR CERTAIN SOLVENTS

The Agency has identified treatment standard concentration levels for certain solvent wastes which must be met before the wastes can be land disposed. These treatment standards are based on the mobility, toxicity, and persistence of the waste (as well as the effects of solvents on liners and the mobilization of other wastes) and the ability of treatment technologies to remove, destroy, or immobilize the hazardous constituents in the wastes.

2.2.1 Solvents of Concern

Treatment standards were proposed in the 14 January 1986 Federal Register for the following spent solvents and commercial chemical products, off-specification commercial chemical products, manufacturing intermediates, and spill residues:

> F001--The following spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; all spent solvent mixtures/blends used in degreasing containing, before use, a total of 10 percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F002, F004 and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
>
> F002--The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,3-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; all spent solvent mixtures/blends containing, before use, a total of 10 percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F001, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
>
> F003--The following spent nonhalogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol;all spent solvent mixtures/blends containing solely the above spent nonhalogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above nonhalogenated solvents, and a total of ten percent or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.

F004--The following spent nonhalogenated solvents: cresols and cresylic acid, and nitrobenzene; all spent solvent mixtures/blends containing, before use, a total of 10 percent or more (by volume) of one or more of the above nonhalogenated solvents or those solvents listed in F001, F002, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.

F005--The following nonhalogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine; all spent solvent mixtures/blends containing, before use, a total of 10 percent or more (by volume) of one or more of the above nonhalogenated solvents or those solvents listed in F001, F002, and F004; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.

The solvent waste constituents of concern and their respective hazardous waste code numbers are:

P022-carbon disulfide
U002-acetone
U031-n-butyl alcohol
U037-chlorobenzene
U052-cresols and cresylic acid
U057-cyclohexanone
U070-o-dichlorobenzene
U080-methylene chloride
U112-ethyl acetate
U117-ethyl ether
U121-trichlorofluoromethane
U140-isobutanol
U154-methanol
U159-methyl ethyl ketone
U161-methyl isobutyl ketone
U169-nitrobenzene
U196-pyridine
U210-tetrachloroethylene
U211-carbon tetrachloride
U220-toluene
U226-1,1,1-trichloroethane
U228-trichloroethylene
U229-xylene

EPA has established immediate effective dates for all but three of the categories of solvent wastes subject to the 14 January 1986 proposed rulemaking. These three excepted categories are solvent-water mixtures (wastewaters) containing less than 1 percent (10,000 ppm) of total organic constituents and less than 1 percent (10,000 ppm) of total solids, inorganic sludges and solids containing less than 1 percent (10,000 ppm) total organic constituents, and solvent-contaminated soils. The Agency has proposed a

2 year national variance for these solvent wastes based upon a determination that the capacities of alternative treatment technologies capable of achieving the treatment standards for these wastes (wastewater treatment units and incinerators), in conjunction with the capacities of alternative recovery and disposal technologies, are insufficient to accomodate the quantities of these solvent wastes currently managed in land disposal units. Schedules have yet to be established for several other P and U Code solvents and other low molecular weight organics.

2.2.2 Proposed Treatment Standards

The legislative history of the 1984 Amendments to RCRA indicates that a waste may be restricted from land disposal not only on the basis of hazards posed by its inherent toxicity, but also because of its ability to degrade clay and synthetic liners and to mobilize relatively nonmobile hazardous constituents, when co-disposed with other hazardous waste. Since solvents exhibit these characteristics, the Agency has considered these overriding factors in developing treatment standards for solvents.

EPA has determined that a number of technologies are applicable to the treatment/recovery of solvent wastes, including biological degradation, steam stripping, carbon adsorption, distillation, incineration, and fuel substitution. The Agency is identifying acceptable technologies for each solvent waste based upon the wastes physical form, the specific solvent constituents they contain, and the concentrations at which such constituents are present. Although final evaluations have not yet been completed, preliminary results indicate that these treatment technologies do not pose total risks to human health and the environment greater than those posed in the direct land disposal of most categories of the solvents wastes subject to the proposed rulemaking.

Table 2-2 shows the technology-based treatment levels and the proposed treatment standards for each solvent constituent in waste codes F001 through F005 wastes.

TABLE 2.2. PERFORMANCE ACHIEVED BY TREATMENT TECHNOLOGIES (mg/liter)

	Treatment Technology				
Constituent	Steam stripping	Carbon adsorption	Biological treatment[1]	Treatment combination	Fuel substitution/ incineration
Acetone			0.052[2]		0.052[2]
n-Butyl alcohol			0.100[2]		0.100[2]
Carbon disulfide					0.010[2]
Carbon tetrachloride			0.010		0.010
Chlorobenzene			0.292	0.062[3]	0.020
Creosols		0.62	0.100[2]		0.100
Cyclohexanone			0.100[2]		0.100[2]
1,2-Dichlorobenzene			0.302	0.053[3]	0.010[2]
Ethyl acetate			0.100[2]		0.100[2]
Ethylbenzene	0.200		0.010		0.100[2]
Ethyl ether			0.100[2]		0.100[2]
Isobutanol			0.050[2]		0.100[2]
Methanol			0.0100[2]		0.050[2]
Methylene chloride	0.109		0.011		0.010
Methyl ethyl ketone			0.050[2]		0.050
Methyl isobutyl ketone			0.010[2]		0.010[2]
Nitrobenzene		0.027	0.010	0.026[3]	0.010[2]
Pyridine			0.500[2]		0.500[2]
Tetrachloroethylene			0.010		0.010
Toluene	0.036	0.016	0.066	0.230[3]	0.010
1,1,1-Trichloroethane	0.457				0.010
1,1,2-Trichloro-1,2,2-trifluoroethane	0.457[2]				0.010[2]
Trichloroethylene	0.019		0.011		0.010
Trichlorofluoromethane	0.457[2]				0.010[2]
Xylene				0.005[4]	0.010[2]

Source: Federal Register Vol. 51, No. 9, January 14, 1986. Table 11, Page 1722.

(1) Includes activated sludge, trickling filters, and aerated lagoons.
(2) Estimated values.
(3) Activated sludge followed by granulated activated carbon adsorption.
(4) Granulated activated carbon followed by steam stripping.

SECTION 3.0

CURRENT INDUSTRIAL SOURCES, GENERATION, AND MANAGEMENT ACTIVITIES FOR SOLVENT WASTES

3.1 INDUSTRIAL SOURCES OF WASTE SOLVENTS

3.1.1 Wastes Considered in Study

The primary purpose of this document is to summarize available information regarding treatment of priority solvents subject to the land disposal ban effective 18 November 1986. Knowledge of current waste management practices and solvent waste characteristics are necessary to determine the applicability of these various technologies. Some discussion of these factors for other solvents and low molecular weight organic compounds has been included since it is recognized that they will often be amenable to the same treatment techniques. Wastes containing these low molecular weight organic, often ignitable compounds, will compete with priority solvents for available treatment capacity as they become subject to land disposal restrictions.

3.1.2 Sources of Solvent Wastes

Priority solvent usage rates are summarized in Table 3.1.1, distinguishing between use as a solvent, consumptive use as a chemical intermediate, and use in the formulation of consumer products. Solvent use is summarized below, first in terms of the major solvent using industries, and then by individual priority solvent. Unless otherwise indicated, demand, export and use data were obtained from the most recent chemical profiles issued by the Chemical Marketing Reporter.[1]

TABLE 3.1.1. CONSUMPTION OF MAJOR SOLVENTS (10^6 LBS/YEAR)

	Use as a solvent										
Solvent classification	Coatings	Adhesives	Inks	Degreasing	Process solvent	Other	Total solvent use	Nonsolvent use	Export	Total demand	Percent used domestically as solvent
Halogenated (RCRA)											
Perchloroethylene	4	6		196		349[1]	555	363	43	865	64
1,1,1-Trichloroethane	12	60		378	36		486	72	42	600	81
Methylene chloride				39	132	113[5]	284	157	49	490	58
Fluorocarbons				111[3]	37[3]		148	880	32	1,060	14
Trichloroethylene	7	0		136			143	10	17	170	84
Chlorobenzene					113		113	155	0	268	42
O-Dichlorobenzene				5	7		12	35	0	47	25
Chloroform					0-10[3]		0-10[3]	312-412[3]	13	425	0-2
Carbon tetrachloride				0-10[3]			0-10[3]	610-620[3]	40	660	0-2
Subtotal:	23	66	--	870	330	462	1,751	2,598	236	4,585	38
Nonhalogenated (RCRA)											
Xylene	425	67		26	62	78	658	28,969		29,627	2
Toluene	358	71	65	31	35		560	6,040		6,600	8.5
Methyl ethyl ketone	308	78	22		156		464	23	73	560	83
Methanol	113			53	146	107	419	7,335[2]	--	7,754	5
Acetone	185			22	121		328	1,515	87	1,930	17
n-Butanol	138	0		7	0.54		199	1,284	112	1,595	12
Ethyl acetate	90				18	29	136	4	79	220	62
Methyl isobutyl ketone	99	0-10	0-10		12-27[3]		121-138[3]	0-10[3]	14	152	80-91
Ethyl benzene						54	54	7,146		7,200	0.8
Isobutanol	26				20		46	120	9	175	26
Cresols				8		24	32	88	13	133	24
Cyclohexanone	0	0	0	0	0		5-25		575-595[3]	600	1-4
Nitrobenzene					19		19	946	--	965	2
Benzene	0			0-30			0-30	445[3]	15	1,460	0-1
Subtotal:	1,742	221	92	162	551	292	3,076	54,916	987	58,971	5.2
Total RCRA solvents	1,765	287	92	1,032	881	754	4,827				
Other organic solvents (non-RCRA)[4]	1,653	--	--	813	1,129	208	3,361	--	--	--	--
Total solvent usage	3,418	287	92	1,845	2,010	962	8,180	--	--	--	--
% halogenated (RCRA)	0.7	23.0	0	47.2	16.4	48.0	21.4	--	--	--	--
% nonhalogenated (RCRA)	51.0	77.0	100.0	8.8	27.4	30.4	37.5	--	--	--	--

[1] Dry cleaning.
[2] Automotive solvent chemicals - 278.
[3] Estimated.
[4] Includes ethanol, isopropanol, special napthas, ethylene glycols, hexane and mineral spirits. Excludes use of ethanol as a solvent in consumer applications.
[5] Paint stripper.

Sources: Reference Nos. 1 through 7.

Solvent consumption is shown in Table 3.1.2 by industrial end use category. Of total priority solvent consumption, 64 percent is represented by nonhalogenated organics. These are widely used by the paint and allied products industry (e.g., as ingredients and wash solvents) and in cold cleaning applications. Conversely, halogenated organics are primarily used in vapor degreasing, cold cleaning and dry cleaning.

The top 20 industries generating priority solvent waste streams regulated under RCRA in 1981 are shown in Table 3.1.3. These data were compiled from an EPA nationwide survey of hazardous waste generators which is discussed in detail in Section 3.3. Small quantity generators, which were excluded from this survey, include many degreasing, coating, and dry cleaning operations. Number of generators and waste quantities for these firms are also discussed in Section 3.3 (Table 3.).

Waste Solvents from the Paint and Allied Products Industry--

The paint and allied products industry represents the largest solvent end use in the U.S. with over 98 percent of its priority solvent consumption accounted for by nonhalogenated solvents. Xylene, toluene, MEK, and acetone are the most widely used materials, while chlorinated solvents (e.g., 1,1,1,-TCE) find wide use only in adhesives (Table 3.1.1). Solvent consumption in the industry is on the decline primarily as a result of process and product changes in response to environmental restrictions. Solvent consumption declined 10 percent during the 1970's and early 1980's as the industry shifted towards high-solids, powder, radiation-curable, and water-based coatings.[3,9] Solvent consumption can be expected to decrease even more rapidly in response to land disposal restrictions. Aliphatics and aromatics will lose market share to oxygenated solvents (e.g., ketones, esters, alcohols, glycols) to meet emissions and disposal standards and the more demanding viscosity requirements of high solids systems.[3] Similarly, a shift from solvent based to water borne or UV curable inks and water based adhesives will occur, reducing overall solvent consumption in these applications. However, halogenated solvents will gain market share in the growing adhesives industry relative to nonhalogenated solvents, which present handling problems as a result of their flammability.

TABLE 3.1.2 PRIORITY SOLVENT INDUSTRIAL END USES

Use category	Percent of use category by solvent type		Percent of solvent type by use category		Percentage of total RCRA industrial solvent usage
	Halogenated	Nonhalogenated	Halogenated	Nonhalogenated	
Paint/coatings	1.3	98.7	1.3	56.8	36.7
Vapor degreasing/cold cleaning	84.3	15.7	49.7	5.3	18.9
Process solvent	37.5	62.5	18.8	18.0	18.4
Dry cleaning	100.0	0.0	19.9	0.0	9.5
Adhesives	23.0	77.0	3.8	7.3	6.0
Industrial paint stripper	100.0	0.0	6.5	0.0	2.4
Inks	0.0	100.0	0.0	3.0	2.0
Miscellaneous	100.0	0.0	0.0	9.6	6.1
Total industrial uses	36.3	63.7	--	--	--

Source: References Nos. 1 through 7.

TABLE 3.1.3. TOP 20 INDUSTRIES GENERATING SOLVENT WASTES

No. of estab.[a]	SIC code	SIC description	Weighted number of solvent waste streams	
			Halogenated solvents[b]	Nonhalogenated solvents[b]
2145	2851	Paints and Allied Products	105	1,436
1160	2869	Industrial Organic Chemicals	327	654
1529	2821	Plastics Materials	215	536
4287	3471	Plating and Polishing	471	176
541	2833	Medicinal, Botanical Products	137	323
2902	3479	Metal Coating and Allied Services	136	279
4656	3662	Communication Equipment	186	225
4151	3714	Motor Vehicle Parts	241	161
393	9711	National Security	166	178
337	3721	Aircraft Equipment	107	230
15490	3079	Plastic Products, Miscellaneous	120	201
2237	3674	Semiconductors	93	194
2563	2899	Chemical Preparations	85	189
6506	7391	Research & Development Labs	103	163
560	3411	Metal Can Fabrication	35	154
1040	3711	Motor Vehicle Bodies	57	127
32	2067	Chewing Gum	57	87
861	2879	Agricultural Chemicals	59	85
5392	3679	Electronic Components	96	40
235	3951	Pens & Mechanical Pencils	66	59
57017				

[a] Number of establishments based on Dun's Marketing Services, a company of Dun & Bradstreet Corp., 1983 Standard Industrial Classification Statistics.

[b] Information on generators taken from 1981 data (National Survey of Generators).

Source: Engineering Science Reference No. 8.

Data on specific waste solvent streams from the paint and allied products industry has been presented in the literature.[10,11,12] These indicate that solvent concentration varies from over 90 percent to trace levels depending on waste source and treatment methods applied. Solvent-bearing coating and ink wastes originate primarily from cleaning operations on tanks and equipment following color or other process changes. These wastes typically consist of a blend of solvents with solids concentrations of up to 10 percent before recovery or disposal is required.

Off-spec materials constitute a minor source of waste since much of this product can be reused in lower grade products. Solvent concentrations reflect those found in saleable products (e.g., up to 42 percent in paints).[13]

A 1977 EPA study of the paint and coatings manufacturing and factory applied coatings industries estimated that approximately 95 percent of the hazardous solvent generated is contained in spent cleaning solutions as summarized in Table 3.1.4. These data suggest that overall, 1 percent of solvents consumed by the paint and allied products industry ultimately results in waste material requiring disposal which is, on average, 21 percent solvent by weight. However, solvent recovery has increased from approximately 35 percent in 1977[10] to 66 percent in the early 1980's (see Section 3.2). Thus, on average, solvent wastes currently land disposed will tend to be less concentrated than these data suggest. Instead they will tend to have higher concentrations of non-solvent materials such as resins, extenders, driers, anti-skinning agents) and contaminants; e.g., dirt, oil, grease.[11] Recovered solvents often find re-use as wash solvents as opposed to use in product formulations unless they are recycled in a manner (e.g., fractionation) which enables them to meet more strict product specifications.

Waste Solvents from Degreasing Operations--

Degreasing is usually employed to remove oils, greases, waxes, lubricants, tars, water and other foreign substances from metal surfaces and other materials. Solvent cleaning operations are carried out in three basic types of equipment; cold cleaners, open-top vapor degreasers, and conveyorized degreasers. Cold cleaners account for all the nonhalogenated solvents used in

TABLE 3.1.4 HAZARDOUS SOLVENT WASTE GENERATION IN THE PAINT AND COATINGS MANUFACTURING AND FACTORY APPLIED COATINGS INDUSTRY

	Solvent waste generation[a] (tons/year)	Percent of waste which is solvent	Percent of total solvent constituents in waste
Cleaning wastes	80,261	22.5	95.2
Off-specification material	5,051	5.9	4.2
Spills	5,438	2.0	0.6
Total	90,750	21.0	100.0

[a] Weighted by a factor of 1.14 to reflect estimates of solvent consumption provided in Table 3.1.1.

Source: US EPA 1977. Reference No. 10.

degreasing and about one third of the halogenated solvents.[2] The remaining two-thirds is used in 21,000 vapor and 3000 conveyorized degreasers[4] in a ratio of approximately two to one.[3] 1,1,1-trichlorethane is the most widely used degreasing solvent followed by fluorocarbons, trichloroethylene and perchlorothylene (Table 3.1.1).

Cold cleaning solvents are recycled or disposed when they become contaminated with approximately 10 percent foreign matter by weight or when cleaning efficiency is otherwise inhibited due to a reduction in solvent power.[14] Vapor decreasing solvents are recycled or disposed when they become 15 to 30 percent contaminated, when the boiling point reaches 5 to 10°F above the pure solvent boiling point,[12] or when solids settling and buildup impairs heat transfer.[14] Fabric scouring solvents are typically recycled on a continuous basis through distillation and decanting. Degreasing wastes are generally amenable to recovery unless contaminants include resinous or polymerizable compounds which will foul heat transfer surfaces. Alternatively, wastes may not be recycled for reuse if stringent product purity specifications cannot be met; e.g., using recovered solvent in applications such as electronic circuitry or printed circuit boards.

Table 3.1.5 summarizes waste generation rates as a fraction of solvent consumption for various cleaning apparatus.[2] These data are from 1979 operations, which was prior to the upgrading of emissions control equipment in many degreasers. Thus, it is likely that the fraction of solvent which becomes waste is higher than the values presented here. However, these data can be applied to current solvent usage rates to estimate the quantity of solvent and potentially ignitable waste which originates from degreasing and paint stripping operations. Using the solvent usage rates provided in Table 3.1.1 and their distribution between types of degreasing applications,[1,2] the data suggest an annual generation of 388 million pounds of spent cold cleaning solvent waste (80 percent halogenated), 87 million pounds fabric scouring (77 percent halogenated) and 109 million pounds of halogenated vapor degreasing waste. If, on average, 75 percent of the material is recovered, this results in 146 million pounds of oily still bottoms (55 percent oil).

TABLE 3.1.5. WASTE SOLVENT GENERATION BY TYPE OF DEGREASING OPERATION[a]

Degreasing operation	Total solvent consumption, that becomes waste solvent, %[a]	
	Range	Average
Cold cleaners:		
Manufacturing (44 percent)	40 to 60	50.0
Maintenance (56 percent)	50 to 75	62.5
Open top vapor degreasers	20 to 25	22.5
Conveyorized vapor degreasers	10 to 20	15.0
Fabric scourers[b]	40 to 60	50

[a] Source: Reference No. 2.

[b] Assumed to be a conveyerized cold cleaner.

Total solvent consumption in metal degreasing is expected to grow less than 1 percent per year because of improved solvent conservation through equipment modification and recycling.[3] Also, industry surveys report a shift towards the use of acid-alkali detergent cleaners for degreasing, reducing industry reliance on more toxic organic solvents.[9] However, lower toxicity halogenated compounds such as 1,1,1-TCE and PERC will maintain or increase their market share in metal cleaning applications.[3]

Waste Solvents from Dry Cleaning--

The EPA estimates that approximately 70 percent of the 40,000 dry cleaners in the country use 349 million pounds of perchloroethylene (PERC) annually while 30 percent use petroleum fractions and less than 1 percent use F-113.[4] Another source estimated this distribution to be 85, 15 and 1 percent, respectively.[15] PERC's moderate cost, low flammability, high stability, high solvency, and high vapor density make it an efficient, easily recoverable solvent in this application.

Dry cleaning wastes consist of spent solvent contaminated with oil, lint, dirt and detergent. These wastes are generated in the form of distillation residues or spent filter cartridges which contain roughly 60 and 50 percent solvent, respectively.[15] Some large dry cleaning operations are equipped with solvent recovery systems such as distillation units, "muck" cookers, or steam strippers which can reduce solvent content in distillation bottoms from 60 percent to 1 percent solvent.[15,16] The International Fabricare Institute estimates that the average facility equipped with conventional filter cartridge and distillation systems generates 45 gallons of solvent containing waste each month (29 gallons of filtration residues) while facilities with secondary recovery systems (e.g., steam distillation, cookers) generate 22 gallons monthly.[15] These estimates are in good agreement with other industry surveys.[17,18] Data indicate that secondary recovery of dry cleaning wastes is not frequently practiced onsite[15] or offsite[11,18] due to the poor economics associated with small quantity waste generation.

3.1.3 Halogenated Organic Solvent Usage in Industry

Perchloroethylene (PERC)--

PERC is the most widely used halogenated solvent with a total annual industrial solvent consumption of 555 million gallons. PERC solvents are primarily used in the dry cleaning (56 percent) and textile processing industries (24 percent) (e.g., fabric scouring, carrier solvent for fabric finishes and water repellants and sizing and desizing operations) because of its high cleaning power, low toxicity, nonflammability, and stability. The EPA estimates that 70 percent of all dry cleaners used 349 million gallons of PERC in 1983 which represents a majority of the industry's solvent usage.[4] Other solvent applications include use in metal degreasing (10 percent) and coatings/adhesives (1 percent). PERC is used in about 15 percent of the vapor degreasers nationwide,[12] but is not more widely applied due to its high boiling point relative to other degreasing solvents. It is used when high temperatures are required to remove high melting waxes and grease, when long cleaning cycles are required,[2] when higher cleaning efficiency is required, or when water is present on part surfaces.[12]

Nonsolvent uses of PERC include use as a chemical intermediate (42 percent), primarily in the production of fluorocarbon F-113, and export (5 percent). Zero growth is expected for PERC with greater recycling in dry cleaning and metal cleaning offsetting increases in demand for F-113 in the electronics industry.

1,1,1-Trichloroethane (1,1,1-TCE)--

Demand for 1,1,1-TCE was 600 million lbs/yr of which 7 percent was exported and 81 percent was consumed domestically as a solvent. The primary solvent uses of 1,1,1 TCE are cold cleaning (41 percent), vapor degreasing (22 percent), adhesive formulations (10 percent), electronics equipment cleaning and process solvent (6 percent), and coatings (2 percent), as well as nonsolvent uses in adhesive applications (7 percent). It is the most widely applied degreasing solvent currently in use. Growth is forecast at 2 percent per year which should outperform most other chlorinated solvents. It replaced trichloroethylene in many metal cleaning applications during the 1970's due to its similar characteristics (nonflammable, suitable evaporation rate, medium solvency), lower toxicity, and lower temperature of parts on removal from degreasers.[12] 1,1,1-TCE is available in uninhibited and inhibited grades using such stabilizers as nitromethane, methylpyrole, 1,4-dioxane, butylene oxide, 1,3-dioxolane and secbutyl alcohol.[3] Improperly stabilized, 1,1,1-TCE can decompose in the presence of aluminum, zinc,[2] or magnesium.[12]

Methylene Chloride (MC)--

MC is a nonflammable, noncorrosive, high solvency petrochemical which is used as a solvent in nearly 60 percent of its applications. It is most widely used as a solvent in paint removal for both industrial and consumer applications (23 percent) chemical processing (e.g., plastics and fiber processing), as an extraction solvent in food processing and for oil dewaxing (20 percent) metal degreasing (8 percent, roughly 80 percent in cold cleaning operations), and electronics (7 percent). Nonsolvent uses include aerosols (20 percent), urethane foam blowing agents (5 percent)[1], a vapor pressure depressant in consumer products and manufacture of polycarbonate insecticides and herbicides.[11] An additional 10 percent of MC is exported. MC is used in the urethane foam industry to clean foam heads and lines between production runs.[11]

MC has been declining in domestic consumption since the late 1970's due to regulatory pressures. It is expected to continue to decline by 1 to 2 percent per year despite advantages over other solvents in several of its applications. In degreasing, it may be used to remove polymer residue (high solvency) or for cleaning heat sensitive parts (low boiling point). However, its low boiling point and consequent low volume of condensate generated may preclude its use where high cleaning efficiency is required. Low operational costs compared to PERC and higher stability in the presence of water compared to 1,1,1-TCE maintain its competitiveness in the degreasing market.

Fluorocarbons--

Fluorocarbons include a variety of fluorinated aliphatics, among them F-11 (trichlorofluoromethane), F-12 (dichlorodifluoromethane) and F-113 (1,1,2-trichloro-trifluoromethane) which are RCRA solvents. Solvent uses account for only 14 percent of demand and consist primarily of F-113 used in specialized solvent cleaning applications in the electronic, aerospace, and optical industries.[3] Similar to methylene chloride, fluorocarbons are suitable for removing polymer residue and for cleaning heat sensitive parts. Their higher cost is offset by higher vapor densities which result in less diffusion of vapors from the degreasers and larger volumes of condensate which make them more suitable for cleaning.

Proprietary mixtures of F-113 with solvents such as acetone, ethanol, methylene chloride, and chloroform have found uses for cleaning fluxes from printed circuit boards, electrical relays, missile guidance systems, electrical meters, hearing aids, and semiconductors.[5] F-113 is preferred relative to other solvents as a result of its minimal attack on paints, gaskets and wire insulation.[3] A small amount of F-113 is also used in the dry cleaning industry (less than 1 percent of dry cleaners).[4,16]

The major use for F-12 is in air conditioning and refrigeration which, combined with F-22, accounts for 39 percent of flourocarbon use. F-11 is primarily used as a foam blowing agent (17 percent of total use). Other nonsolvent uses include resin intermediates and aerosol propellants. Fluorocarbon demand is expected to increase 4 to 5 percent per year with the highest growth experienced by F-113 in electrical and electronic applications as a substitute for chlorinated solvents.

Trichloroethylene (TCE)--

TCE is used primarily as a degreasing solvent which account for 80 percent of total demand. Other solvent uses include paints, coatings and general solvent applications (4 percent) while 10 percent is exported and 6 percent is consumed as a chemical intermediate (pesticides and herbicides). High purity, low residue grades are used for cleaning critical electronic components, chemical synthesis, and extraction processes for wax, oils and resins. Stabilized grades are used for vapor degreasing and other cleaning operations and have been developed to remain effective through repeated distillations and degreasing of aluminum.[5] Demand is expected to decline 2 to 4 percent per year as a result of solvent recycling practices and regulatory pressures. However, TCE has superior dissolving properties and is technically preferred to tetrachloroethylene in vapor degreasing because of its lower boiling point.[11]

Chlorobenzene--

Chlorobenzene is used as a solvent in pesticide formulation and toluene di-isocyanate processing[1] and, to a lesser extent, as a degreasing agent, dye assist agent, and synthetic rubber solvent for dipping applications.[5] These represent 42 percent of current demand. Nonsolvent uses include production of nitrochlorobenzenes (32 percent) and diphenyl oxide and phenylphenols (15 percent). Demand is expected to decline 3 percent per year or more, primarily due to reduced consumption in pesticides.

o-Dichlorobenzene--

o-Dichlorobenzene is used as a solvent in 25 percent of its applications, primarily in the phosgenation of mono and diamines to toluene di-isocyonate (15 percent) and in cold cleaning operations (10 percent). The latter include paint removing, engine cleaning, and de-inking.[5] It's primary nonsolvent use is in the synthesis of pesticides (65 percent) including 3,4-dianiline in dyestuff manufacture (5 percent) and as a heat transfer agent.[5] Demand is expected to decline 1 percent per year.

Chloroform--

The vast majority of chloroform is used as a chemical intermediate in the production of Fluorocarbon F-22 (93 percent). Exports account for 3 percent of demand and the remaining quantity (4 percent) is divided between the following miscellaneous uses: manufacture of polytetrafluoroethylene, preparation of dyes and pesticides, extractant in the production of penicillin vitamins and flavours, a general solvent for adhesives, resins, pharmaceuticals and pesticides, as a solvent for removing fat from waste products, and as a dry cleaning spot remover.[1,5,19] One source reported that chloroform was widely used as a solvent in the lacquer industry but did not substantiate this claim.[20] Total use as a solvent is probably less than 10 million pounds annually.

Carbon Tetrachloride--

Carbon tetrachloride's use as a solvent is negligible. It is an ideal extraction solvent (low surface tension, high density, and good solvency) for oils, waxes and fats, particularly those derived from animal and vegetable sources, and has found solvent use in degreasing, shoe and furniture polishes, paints, lacquers, printing inks, floor wastes, stains,[3] and as a grain fumigant.[1] However, regulatory pressures have since reduced its uses to that of a chemical intermediate, primarily in the production of Fluorocarbons F-11 and F-12 (91 percent). The bulk of the remaining carbon tetrachloride produced in the U.S. is exported (6 percent) or used in other nonsolvent chemical intermediate applications(3 percent). Similar to chloroform, total use as a solvent probably does not exceed 10 million pounds annually.

3.1.4 Non-halogenated Organic Solvent Usage in Industry

Xylene--

Xylenes used for solvent applications are mixed xylenes which have been depleted in ortho- and para-xylene. These represent only 1.9 percent of total xylene demand in the U.S.[3] Xylene is less expensive than most solvents and evaporates rapidly. Similar to other aromatics, it is able to solubilize resins and lacquers and is consequently widely employed in the paint and coatings industry, e.g., wash solvent, stripping and general solvent use in formulations. This accounts for approximately 58 percent of mixed xylene use. Other solvent uses include adhesives (9 percent), process solvent (9 percent), agricultural sprays (9 percent)[1] cold cleaning and fabric scouring (4 percent)[2] and miscellaneous applications (2 percent) such as printing inks.[1] Total mixed xylene demand is expected to decline by more than 2 percent per year.

Nonsolvent uses of xylenes include production of dimethyl terephthalate and terephthalic acid using p-xylene (92.6 percent), phthalic anhydride with o-xylene (2.5 percent), gasoline (2.8 percent), isophthalic acid and, to a lesser extent, isophthalonitrile with m-xylene (0.2 percent). Growth for nonsolvent uses should bs 3 to 4 percent per year.

Toluene--

Chemical uses of toluene are estimated to require 6600 million pounds in 1986, of which 8.5 percent is used in solvent applications. Of this, 64 percent is consumed in paints and coatings and 36 percent in formulating adhesives, inks (rotogravure) and pharmaceuticals with minor uses such as chemical processing and cold cleaning (e.g. varnish remover). Toluene is relatively fast drying and inexpensive. It is used along with other aromatics as a wash solvent and for thinning resins which are difficult to solubilize by aliphatics (e.g. short-oil alkyds, vinyl alkyds, phenolics, chlorinated rubber coatings, lacquers).[10,14] Use of toluene as a solvent has decreased in recent years from estimates of 625 million pounds in 1980 to 560 million pounds in 1986.[20] As a result of continued regulatory pressures it will probably continue to decline at roughly 2 percent per year.[3] However, other chemical uses have been increasing at nearly 5 percent per year since 1981. These nonsolvent uses include the production of benzene (71 percent), toluene di-isocyanate (9 percent), benzoic acid (2 percent), benzyl chloride (1 percent), and other chemicals (0.75 percent).[1]

Methyl Ethyl Ketone (MEK)--

The majority (83 percent) of MEK is used as a solvent or exported (13 percent). Primary solvent uses include vinyl, nitrocellulose, acrylic and other coatings (55 percent), a solvent in adhesives (14 percent), magnetic tapes (6 percent) printing inks (4 percent), and lube oil dewaxing (4 percent). Nonsolvent uses are minor and consist of applications as a chemical intermediate (4 percent). Other possible uses include vegetable oil extraction, azeotropic distillation in refineries,[11] and cold cleaning.[2]

MEK is rarely, if ever, used in paints since it is relatively expensive. However, its rapid drying capability and strong solvency for lacquer binders (i.e., nitrocellulose, acrylics, vinyls, etc.) make it the preferred solvent for thinning of epoxy and PVC[10,14] coatings and occasional use as a stripper.[6]

Growth in MEK demand is expected to be 3 percent per year since its high solvency has allowed it to maintain its coatings market share. However, increased recycling in the magnetic tape and printing industries will reduce demand in these sectors.

Methanol[3]--

Low price, high purity and excellent dissolving properties are responsible for making methanol one of the most widely used solvents. However, only 5 percent of methanol consumption consists of use as an industrial solvent. Of this, methanol is most widely used as a process and wash solvent in the production of paints and coatings (27 percent), for cleaning and as a component of paint remover (13 percent), as a chemical process solvent in the preparation of pharmaceuticals (35 percent), and as a solvent for inks, coated fabrics, and other applications (25 percent). Total solvent use should expand at a rate of 2.2 percent annually, with growth in most applications somewhat offset by stable demand in the paint and coatings industry.

Nonsolvent uses constitute the majority of methanol consumption (95 percent). These include production of formaldehyde (34 percent), acetic acid (8 percent), chloromethanes (7 percent), methylamines (6 percent), windshield cleaner and deicer (4 percent), methyl methacrylate (5 percent), methyl tertiary butyl ether (5 percent), and other uses (26 percent). Methanol demand is expected to be high in nonsolvent uses (5.5 percent annually) led by growth in acetic acid, MTBE, and several of the other chemicals. Demand for formaldehyde, the largest methanol derivative, is also expected to be strong due to growth in the building and construction industry.

Acetone--

Approximately 17 percent of acetone is used in solvent applications. These include coatings (10 percent) and miscellaneous uses (7 percent) such as a spinning solvent in the manufacture of cellulose acetate fiber (5 percent),[1] a solvent in the manufacture of inks,[11] smokeless powder, cements and artificial leather, dewaxing of lubricating oils,[3] and cold cleaning.[2] In the coatings industry it is used in varnishes, lacquers, thinners, and as a wash solvent.[11] Most acetone is used in nonsolvent applications including the manufacture of methacrylates (33 percent), methyl isobutyl ketone (10 percent), bisphenol A (9 percent), aldol derivatives (7 percent), vitamins, pharmaceuticals and cosmetics (6 percent), and methyl isobutyl carbinol (2 percent). Despite its preferred use in high solids coatings, acetone use in coatings will probably decline slightly as the industry shifts toward water-based and powder coatings.[1] Other solvent uses may increase 2 percent per year[3] and nonsolvent uses are expected to increase 3 percent per year.

n-Butanol--

Approximately 12.5 percent of n-Butanol is used in solvent applications with 9 percent in paints, coatings and adhesives and 3.5 percent as a process solvent[1] and cold cleaner.[2] Process solvents are used in the production of pharmaceuticals, waxes, resins,[3] dyes, and photographic chemicals.[22] Butanol is not a solvent for nitrocellulose but its presence in the solvent mixture of a nitrocellulose lacquer or enamel, or in alkyd/amino enamels, improves flow and leveling during coating application.[5] Other coatings, such as alcohol soluble shellacs may use butanol as a thinning agent. Nonsolvent uses include the production of butyl acrylates and methacrylate (30 percent), glycol ethers (23 percent), butyl acetate (12.5 percent), plasticizers (8 percent), amino resins (5 percent), amines (1 percent), and exports (7 percent).

Demand for n-butanol as a solvent is expected to remain stable but overall growth is projected at 3 to 4 percent per year. n-Butanol based water-borne coatings and adhesives are favored over competing products due to their solubility characteristics. This compensates for the shift to more active solvents in high solids coatings.

Methyl Isobutyl Ketone (MIBK)--

MIBK is similar to MEK in that the majority of the compound (80-91 percent) is used in solvent applications, primarily in the coatings industry. The largest single use is as a solvent in nitrocellulose lacquers (30 percent) with another 36 percent used for various coatings, adhesives, and inks. Its strong solvency, low density, and high electrical resistivity make it a good solvent for high solids coatings such as acrylics, polyesters, alkyds, and acrylic/urethanes.[5] Another significant use (8 percent) is as a rare metal extractant and the remainder is exported (9 percent)[1] or applied in miscellaneous uses such as a solvent in pesticides, pharmaceuticals (tetracyclene antibiotics purification), and use as a denaturant.[5] MIBK is frequently blended with MEK to achieve balanced active solvent characteristics in high solids lacquers and for use as a solvent in low-viscosity vinyl resin solutions.[5]

As with MEK, MIBK is expected to increase in demand by 3 percent per year, as shifts to high solids coatings encourage the increased use of pure ketone formulations at the expense of lower solvency blends.

Ethyl Acetate--

Ethyl acetate is widely used as a solvent, particularly in protective coatings such as nitocellulose lacquers. Excluding exports (36 percent), solvent use accounted for 98 percent of ethyl acetate demand with the remainder being used in chemical synthesis. Coatings accounted for 66 percent of domestic solvent usage, plastics solvents (acrylic and cellulosic polymers) accounted for 13 percent, and use in inks, adhesives, and other applications made up the remaining 21 percent of solvent use. Demand for ethyl acetate has been stalled due to increased production of water-based coatings and the substitution of ketones in place of the less active esters in high-solids coatings. However, since it is a moderate cost, low toxicity solvent which serves mature markets, demand is still expected to increase from 1 to 2.5 percent per year.

Isobutanol--

Isobutanol can be readily interchanged with n-butanol in solvent applications. Solvent end uses consumed approximately 25 percent of isobutanol demand with 14 percent being used in coatings and 11 percent as a process solvent.[3] Coatings which use isobutanol include nitrocellulose lacquers, latexes, acetate exters, urea-formaldehydes, butyl acetates and alcohol soluable shellacs.[11] Demand in these applications is expected to mirror that of n-butanol. Non-solvent uses include production of isobutyl amine herbicides (21 percent), lube oil additives (14 percent), isobutyl acetate production (14 percent), acrylates (4 percent), exports (50 percent) and miscellaneous uses (17 percent).[3] Demand for these diverse non-solvent uses should parallel economic growth.

Cresols--

Cresols are used in the production of magnetic wire as an enamel solvent (18 percent), as an ore flotation agent (6 percent), as an intermediate in the production of phosphate esters (16 percent), resins (16 percent), and antioxidants (16 percent). Miscellaneous chemical intermediate applications (13 percent)[1] include perfumes, herbicides, disinfectants, and use as a textile scouring agent.[22] Six percent of cresol demand is made up of use as a cleaning compound which, together with wire enamel solvents, represents the bulk of cresol use as a solvent. Exports account for the remaining 10 percent of U.S. consumption. Growth of cresols is expected to be 2 percent per year, primarily in the specialty chemicals areas.

Cyclohexanone[5]--

Cyclohexanone is primarily used in nonsolvent applications with the vast majority consumed as an intermediate for adipic acid (50 percent) and caprolactum (45 percent) which, in turn, are nylon intermediates. Cyclohexanone has not captured a significant share of the solvent market due to economics (high boiling, slow evaporation, relatively expensive) but it is an excellent solvent for vinyl resins, cellulose esters, ethyl cellulose, polystyrene, and acrylic resins. It is reportedly used as a solvent for protective coatings, adhesives, inks, cleaning products, magnetic tapes, and pesticides. Its cost is offset by its ability to tolerate large amounts of inexpensive hydrocarbon solvents in the formulation of low cost thinners. Long term demand as a solvent is not expected to increase significantly and cyclohexanone demand for nylon should increase only 1 to 2 percent per year.

Nitrobenzene--

Nitrobenzene is used primarily in the production of aniline (97.5 percent) which is expected to exhibit a growth rate of 6 percent per year. Other nonsolvent uses include production of n-acetyl p-amino phenol. Use as a solvent, which is probably 2 percent or less of total demand, includes the refining of certain lubricating oils and in various Friedel-Crafts reactions.[6] Other reported solvent applications include TNT production, cellulose acetate manufacturing, metal and shoe polish, dyestuff, rubber chemicals and photographic chemicals.[22]

Benzene

Benzene is used as a solvent only in rare cases when it cannot be replaced by less hazardous substitutes; e.g., other aromatics like toluene, xylene.[6]

One source reports use of benzene in dyes, coatings, and photographic materials[22] but it is probably employed as a chemical raw material rather than as a solvent.[10] A 1972 survey of the paint and coatings industry reported less than 9 million pounds per year of benzene consumption.[2] Another source reported 15 million pounds consumed in cold cleaning and another 77 million pounds used in fabric scouring in 1974, representing 0.8 percent of total benzene consumption.[4] It is likely that these solvent uses have declined radically in the intervening years due to regulatory pressures and awareness of benzene's toxicity.

Nonsolvent uses of benzene include production of ethylbenzene/styrene (52 percent), cumene/phenol (22 percent), cyclohexane (15 percent), nitrobenzene/aniline (4.5 percent), detergent alkylate (2.5 percent), chlorobenzenes, maleic anhydride, and miscellaneous chemicals (3 percent), and exports (1 percent). Demand is expected to increase 2.3 percent per year.

3.2 SOLVENT WASTE GENERATION

The most recent evaluation of solvent waste generation, management practices and waste physical forms has been compiled by the U.S. EPA in the form of a background document to support 40 CFR Part 268 land disposal restrictions.[23] This evaluation was based on an updated version of the 1981 National Survey of Hazardous Waste Generators and Treatment, Storage and Disposal (TSD) Facilities Regulated Under RCRA which was performed by WESTAT.[24] In cases where this data was not available, the results of an earlier study performed by Engineering Science[8], formed the basis of this subsection. Specifically, data pertaining to the relative utilization of most management practices by waste category (e.g., ignitables, halogenated solvents, nonhalogenated solvents) and waste physical form (e.g., solid, liquid, sludge) were based on the earlier survey.

The National Survey data was compared with other national, regional and state surveys to develop an overview of solvent waste generation. The results are summarized in Table 3.2.1. The primary difference between waste quantities reported in these surveys is inclusion or exclusion of large quantity, dilute wastewater streams which contain the constituents of concern. For example, the EPA reports that three facilities accounted for 94 percent of solvent wastes treated in surface impoundments.[23] GCA concluded that little confidence can be placed in the reported generation and management figures unless the wastes are analyzed on the basis of physical form or, preferably, waste constituent concentrations. This approach was adopted when possible.

Highlights of the combined analysis of these surveys are summarized below:

- 3 to 5 billion gallons of waste solvents and 1 to 3 billion gallons of ignitable wastes are generated annually, the majority of which is aqueous waste which is treated and discharged by methods which do not constitute land disposal.[8,25,23]
- Approximately 1.5 billion gallons of nonaqueous waste solvents and ignitables are managed at TSD facilities[8] which represent only 19 to 38 percent of the total wastes generated.

TABLE 3.2.1. SUMMARY OF WASTE GENERATION AND MANAGEMENT (MILLIONS OF GALLONS)

Waste activity	Ignitables	Halogenated solvent	Nonhalogenated solvent	Total solvent	Total	Source (Reference No.)
Generation	603	2,572	998	3,570	4,173	8
	--	765	3,812	4,577	--	25
	1,400	--	--	3,200	4,600	23
Management Practices						
Recycling (onsite)	237	121	315	436	673	8
	37	110	275	385	422	26
(offsite)	63	59	51	110	173	8
	26	52	45	97	123	26
Total:	301	179	366	545	846	8
	63	162	320	482	545	26
Deep well injection	14	290	12	302	317	8
	26			291	317	27
Incineration	122	62	133	195	317	8
	56	--	--	32	88	27
Landfill	16	--	--	32	48	23, 27
Surface impoundment (includes all TSD)	--	--	--	1,169	--	23
Waste pile	--	--	--	0.7	--	23
Land application	--	--	--	0.001	--	23
Land disposal (excludes deep-well injection and TS impoundments)	29	38	15	53	82	8
	21	--	--	39	60	27
Treatment (excludes incineration)					1,179	8
Storage					1,408	8
Total TSD	1,240	588	835	1,423	2,663	8
Total TSD (excluding inorganic liquid)	1,157	116	261	377	1,534	8
Actual data reported before extrapolation	447	85	173	258	705	8

- 50 percent of large quantity generators ($\geq$1,000 kg/month) nationwide (7,180 facilities) produce solvent-containing wastes; 43 percent of generators (6,117 facilities) produce ignitable wastes.[24]

- At least 0.55 billion gallons were recycled, of which approximately 80 percent were recycled onsite.[23] However, recycling, particularly onsite activities, is not well defined and, therefore, may differ significantly from this figure.

- Approximately 60 percent of nonaqueous solvents are currently recycled.[8,23]

- 0.12 to over 0.2 billion gallons of solvents and ignitables are recycled offsite with approximately 15 percent of this quantity used as fuel.

- 0.4 billion gallons of waste are land disposed (1.5 billion including storage and treatment impoundments[23]) with the following physical profile:[8]

  - Inorganic liquids: 266 million gallons (<1% TOC, <1% TS)
  - Inorganic sludges: 36 million gallons (<1% TOC, $\geq$1% TS; includes soils)
  - Organic liquids: 36 million gallons ($\geq$1% TOC, <1% TS)
  - Organic sludges: 11 million gallons ($\geq$1% TOC, $\geq$1% TS)
  - Other/unknown: 46 million gallons
  - Solids: 3.4 million gallons (no free liquid)

- Land disposed solvent wastes are currently managed by:[8]

  - Deep well injection: 79 percent
  - Landfill: 15 percent
  - Surface impoundment: 3 percent

These results should be interpreted with caution. The large volume of dilute aqueous wastes which comprise the vast majority of the waste reported above, distorts the perceived disposition of actual solvent constituents. The National Survey questionnaire was structured in a manner which limits the reliability of the data; e.g., generation estimates include possible double counting and preferentially weight halogenated waste quantities relative to nonhalogenated solvent quantities. The waste quantity data itself is not normally distributed which, combined with erroneous reporting of non-RCRA wastes and differences between the current and 1981 definitions of RCRA wastes further limit its reliability. Finally, waste generation and management practices have changed since 1981 due to regulatory changes, heightened awareness of hazardous waste issues, and economic factors. A more detailed discussion of the survey structure and deficiencies can be found in the references.[8,24]

If the inorganic liquid streams are extracted from the National Survey data, a more accurate picture of waste quantity emerges. Physical characteristics are summerized by waste category in Table 3.2.2. As shown, aqueous wastes accounted for only 6.8 percent of known ignitable waste by volume, whereas it accounted for 80 percent of halogenated and 69 percent of nonhalogenated solvent wastes. When weighed by these factors, ignitable wastes account for 63 percent of the nonaqueous waste, while nonhalogenated solvents account for 25 percent and halogenated solvents 12 percent (33 percent of solvents).

This distribution agrees well with that reported in other surveys.[2,38,29,30,31] Ignitable waste quantities ranged from 55 to 58 percent of total solvent/ignitable waste generation while halogenated compounds accounted for 12 to 50 percent of solvent wastes with an average of 30 percent.

Total solvent waste generation estimates provided by ES[8] (3,570 MGY) and the Congressional Budget Office[25] (4,577 MGY) appear to adequately represent the universe of solvent waste generation. More highly concentrated organic and solid wastes handled through recycle, use as a fuel, land disposal (excluding deep-well injection) and incineration represent 22 percent and 17 percent, respectively, of solvent waste generation identified in these surveys.

A third survey which covered a majority, but not all, hazardous waste generating industries, identified 3.0 billion gallons of solvent waste of which 15 percent was handled in nonwastewater systems.[31] Thus, a total national solvent waste generation of 3.5 to 4.6 billion gallons with 15 to 20 percent concentrated solvents is probably in the correct range.

TABLE 3.2.2. PHYSICAL FORM OF WASTE IGNITABLES AND SOLVENTS MANAGED AT TSD FACILITIES (GPY)

Work category	Physical form							
	Solids	Inorganic sludges	Inorganic liquids	Organic liquids	Organic sludges	Miscellaneous[a]	Unknown	Total
Ignitables								
Totals	11,930,825	2,680,816	26,646,844	161,754,587	7,829,073	181,351,105	88,169,305	480,362,555
Percentage	2.48	0.56	5.55	33.67	1.63	37.75	18.35	--
Halogenated solvents								
Totals	1,022,484	18,756,917	314,939,925	33,020,129	23,806,641	474,418	40,946,534	432,967,043
Percentage	0.24	4.53	72.74	7.63	5.50	0.11	9.46	--
Nonhalogenated solvents								
Totals	474,862	157,585	371,126,235	137,403,686	31,269,647	188,044	11,871,670	552,491,729
Percentage	0.09	0.03	67.17	24.87	5.66	0.03	2.15	--
All Ignitables & solvents								
Totals	13,428,171	21,595,318	712,713,004	332,178,392	62,905,361	182,013,567	140,987,509	1,465,821,322
Percentage	0.92	1.47	48.62	22.66	4.29	12.42	9.62	--

[a] Miscellaneous probably consists mostly of organic, sludge, and solid wastes.

Source: Engineering Science, Reference 6.

Although individual constituent codes (i.e., U and P RCRA codes) and mixed codes accounted for roughly 30 percent of the waste streams reported in the National Survey, they contributed only 5.2 percent of the nonaqueous waste volume (2 percent of total volume).[8] D001 represented 98 percent of the nonaqueous ignitable waste volume. Nonaqueous halogenated solvents were dominated by F002 (81 percent) followed by F001 (8 percent), and miscellaneous codes (11 percent). Nonhalogenated nonaqueous solvent waste volume was dominated by F003 (68 percent) followed by F005 (20 percent), F004 (0.1 percent) and miscellaneous (12 percent). In decreasing order of nonaqueous waste volume for all solvents/ignitables we have D001 (441 MGY), F003 (117 MGY), F002 (69 MGY), F005 (35 MGY), F001 (7 MGY), F004 (0.2 MGY) and miscellaneous codes (37 MGY).

Individual constituent (i.e., U and P codes) were frequently reported in the National Survey for wastes which were not off-specification commercial products, spills, or contaminated containers. Thus, they can be used to estimate the relative frequency of wastes generated which contain these compounds. Solvent constituents are ranked in Table 3.2.3 in decreasing order of frequency as they occurred in the National Survey. Their reported waste volumes are also provided for nonaqueous wastes. However, due to the small sample and skewness of the data from which these figures are derived, the frequency of reporting these constituents is probably more indicative of their relative importance than their reported waste volumes.

Table 3.2.3 shows a comparison between use of priority solvents (Section 3.1) and frequency of reporting these constituents in the National Survey. With the exception of perchloroethylene, agreement between these data is generally quite good. This is most likely due to the fact that 55 percent of PERC usage consists of dry cleaning solvent. These firms recycle wastes as part of their process and small firms would not generate enough waste to be considered large-quantity generators (Section 3.1). Excluding dry cleaning use, PERC would drop down to the ninth most-commonly used solvent which would put it more in line with the National Survey waste generation estimate.

Methylene chloride ranked seventh in both studies, but was second highest in waste quantity reported in the National Survey. Methylene chloride is widely used as a paint stripper (40 percent), which would be high in solids

TABLE 3.2.3. RELATIVE RANKINGS OF SOLVENT WASTE CONSTITUENTS

Waste constituent	Frequency of occurrence in National Survey[1]	Waste quantity reported in National Survey in (No. of streams)	Ranking by frequency in National Survey[a]	Ranking by use as a solvent[b]	Ranking by quantity reported in New Jersey[c]
Toluene	1,304	1,439,163 (175)	1	2	1
Xylene	1,074	714,063 (109)	2	1	5
Acetone	970	9,587,153 (131)	3	7	2
Methyl ethyl ketone	970	404,750 (86)	4	5	7
1,1,1-Trichloroethane	880	1,645,496 (117)	5	4	10
Methanol	768	410,116 (115)	6	6	4
Methylene chloride	641	6,481,266 (122)	7	7	3
n-Butanol	451	54,324 (13)	8	8	-
Ethyl acetate	364	188,070 (33)	9	11	-
Trichloroethene	352	41,755 (42)	10	10	9
Methyl isobutyl ketone	348	26,402 (18)	11	12	6
Chloroform	322	85,488 (50)	12	22	-
Tetrachloroethylene	248	111,515 (74)	13	3	11
Isobutyl alcohol	221	35,057 (8)	14	15	-
Benzene	210	384,947 (27)	15	18	-
Cresols	NA	NA	16[d]	16	-
Nitrobenzene	NA	NA	17[d]	17	-
Cyclohexanone	108	-	18	19	-
Fluorocarbons	89	-	19	9	8
1,2-Dichlorobenzene	65	5,367 (34)	20	20	-
Compounds for which use as a solvent was not determined:					
Tetrahydrofuran	163	93,156 (57)			
Pyridine	138	-			
Ethyl ethers	137	-			
Acetonitrile	126	618,369 (18)			
Carbon disulfide	21	292,575 (22)			

[a] Source: Engineering Science analysis of the National Survey TSD Questionnaire, Reference 8.

[b] Source: Section 3.1.

[c] Source: Survey of Waste Management Practices in New Jersey, Reference 30.

[d] Estimated ranking.

content and, therefore, not economically recoverable relative to other solvents. Thus, a significant fraction of this material is probably land disposed, which would preferentially weight this material in a survey which was not specifically designed to measure recycling.

A 1985 survey of hazardous waste in New Jersey[30] determined spent solvent waste quantities by constituent type for offsite wastes containing greater than 10 percent solvent. These are also presented in Table 3.2.3, along with the National Survey and solvent use data. The New Jersey survey generally supports the above observations. Methylene chloride was again ranked high in terms of waste volume. Acetone was also ranked high relative to its reported use as a solvent. This is possibly due to the fact that acetone may find wider use as a wash solvent than was indicated in Section 3.1.

Impact of Regulatory and Other Changes on Waste Generation Estimates--

Since 1981, the definitions of small quantity generators and F001 through F005 wastes have been and are being revised to include more waste under RCRA. Spent solvents which resulted from the use of solvent mixtures were not regulated until April 30, 1985. At this time, the EPA promulgated new regulations covering solvent blends which originally contained 10 percent or more of one or more listed solvents (F001, F002, F004, and F005) or was a blend of F003 solvents.[32] On June 30, 1985, the EPA proposed adding 1,1,2-trichloroethane to the F002 listing and benzene, 2-ethoxyethanol and 2-nitropropane to F005.[33] Finally, on August 1, 1985, the EPA proposed lowering the small-quantity generator exclusion limit from 1,000 kg to 100 kg/month.[34] Thus, given these new definitions, the ES estimates would understate solvent waste generation.

The impact of these regulatory changes on spent solvent generation regulated under RCRA is unclear because it is not known to what extent generators made use of the F001 through F005 solvent mixture loophole. This loophole is potentially significant since a large percentage of solvents are used in blends as opposed to technical grade or pure forms. As an indication of this, over 18 times as much wastes being shipped to Illinois recyclers consisted of hazardous solvent blends relative to single component waste streams.[11] However, available waste characterization data suggests that many firms reported any waste containing hazardous solvents as RCRA wastes, regardless of the strict definition as stated in the RCRA Part 261 provisions.[31]

The impact on projected waste quantities from changes in waste code definitions and small quantity generator requirements can be estimated. A 1985 report on small quantity generators[17] (see Table 3.2.4) concluded that 85,923 MTY of spent solvents and 1,863 MTY of solvent still bottoms were generated by 33,475 and 738 firms, respectively, that produced between 100 and 1,000 kg/month of hazardous waste. Another 17,844 MTY of ignitable wastes were generated by this group. Total quantities of spent benzene, 1,1,2-trichloroethane, 2-nitropropane, and 2-ethoxyethanol solvents from large quantity generators were estimated to be 22,940 MTY and their recovery still bottoms were estimated to be 8,770 MTY.[33] The combined additional organic residues from these sources (137,340 MTY) would add approximately 38 MGY (1.6 to 2.5 percent) to the estimated 1,534 to 2,380 MGY of concentrated wastes currently recycled or land disposed.

3.3 WASTE MANAGEMENT PRACTICES

Most of the following discussion relies on National Survey data which was available from ES.[8] This is compared with more recent survey data and other literature sources to describe current management practices. Characteristics of RCRA priority solvent wastes are summarized in Table 3.3.1 by management practice. These data are discussed in more detail in the following subsections which are devoted to specific waste management methods.

3.3.1 Recycling (Includes Use as a Fuel)

This subsection summarizes quantities of recycled solvent and ignitable wastes by waste code and constituent type, waste characteristics of recycled streams and end uses of recycled solvents.

TABLE 3.2.4. NUMBERS OF SMALL QUANTITY GENERATORS[a] AND WASTE QUANTITY BY WASTE STREAM[b]

Waste type	No. of generators	Waste quantity (MTY)
Solvent wastes		
Spent solvents	33,475	85,923
Solvent still bottoms	738	1,863
Ignitable wastes		
Ignitable paint waste	3,122	4,872
Formaldehyde waste[c]	2,014	5,396
Other ignitable wastes	2,873	7,576

[a] Generators of 100 kg to 1,000 kg of hazardous waste/month.

[b] Source: Reference 27.

[c] Potentially ignitable.

TABLE 3.3.1. CHARACTERISTICS OF RCRA SOLVENT WASTES BY WASTE MANAGEMENT PRACTICE

Waste management practice	Total priority solvent concentration				Percentage of total waste volume			Total waste quantity MT/YR	Total number of wastes	Average waste stream volume MT/YR
	Minimum	Maximum	Mean	Volume weighted mean	Greater than 10% solvent	1% - 10% solvent	Less than 1% solvent			
Boiler	0.40	80.50	37.41	5.64	9.44	1.58	88.97	231,053	61	3,788
Incineration	0.01	80.00	27.57	11.44	18.72	30.14	51.14	124,802	157	795
Landfill	0.0013	35.50	7.42	10.62	36.69	31.15	32.16	109,304	91	1,201
Recovery and Reclamation	0.01	98.00	40.04	8.57	12.22	7.99	79.79	1,190,515	136	8,754
Underground Injection	$7.4\ E^{-6}$	60.00	5.63	0.75	0.20	7.85	91.95	1,500,974	61	24,606
On-site Treatment Tank	$3.4\ E^{-4}$	5.50	0.71	0.52	0.0	8.68	91.32	2,771,207	120	23,093
Surface Impoundment	$1.6\ E^{-4}$	4.00	0.30	0.30	0.0	2.21	97.79	4,888,157	101	48,398
Waste water Discharge	$3.0\ E^{-4}$	10.78	1.06	0.56	1.00	4.53	94.47	6,540,467	221	29,595
All Processes[1]	$7.4\ E^{-6}$	98.00	14.36	1.26	1.72	5.43	92.85	17,360,911	964	18,009

[1] Includes 16 Streams (4,432 MT/YR) Dicharged to Unidentified Private Treatment Works.

Source: Adapted from Industry Studies Data Base. Reference No. 31.

Total quantity of solvent recycling reported in the National Survey is difficult to verify primarily due to lack of data on onsite activities. Where these data exist, interpretation of the results is hindered by the ambiguities surrounding the definitions of RCRA wastes. Whether an onsite waste is considered a hazardous waste prior to recycling, or whether the recycling process is considered to be an integral part of the process from which the waste was derived, is subject to interpretation. For example, solvent refining, polymerization processes and vegetable oil manufacturers annually recycle billions of gallons of solvent internally in their processes which are not considered to be hazardous wastes.[3]

Since the majority of waste solvents are recycled onsite (78[8,26] to 92[3] percent), uncertainties in onsite recycling estimates translate into large errors in total recycling quantity estimates. In contrast, offsite recycling is less subject to the ambiguities which surround onsite activities and has been studied more extensively.

Recycled solvent and ignitable quantities, as reported in the revised National Survey, are summarized in Table 3.3.2. Recycling estimates for ignitable, halogenated solvents and nonhalogenated solvents were 63, 62 and 320 MGY, respectively. Of this, 22 percent (123 MGY) was recycled offsite and 30 percent was halogenated solvents. Although no comparative data on onsite recycling activities was available, offsite recycling has been evaluated by a number of other sources, all of which involved surveying a distinct population and extrapolating to national totals. These estimates resulted in higher projected recycled solvent quantities, ranging from 149[8] to over 240 MGY [References 9,11,18,25,28 and 30]. Thus, it seems probable that the National Survey underestimated recycled waste quantities.

In general, the National Survey showed good agreement with other waste surveys in terms of percentage of solvent recycled and the relative quantities of halogenated versus nonhalogenated solvent recycled. A review of the data [References 3,8,26,31 and 35] show roughly one fourth of all solvent wastes and 60 to 65 percent of nonaqueous wastes are currently recycled. Of this, nearly 30 percent are halogenated solvents (References 3,8,10,11,18,26 and 28).

TABLE 3.3.2. WASTE RECYCLING REPORTED IN THE REVISED NATIONAL SURVEY

Waste category	Waste code	Volume recycled offsite (1,000 gal/yr)	Volume recycled onsite (1,000 gal/yr)	Percent recycled onsite	Total recycled waste (1,000 gal/yr)
Ignitables	D001	26,140	36,664	58.3	62,804
Halogenated solvents	F001	32,155	10,011	23.7	42,166
	F002	7,029	95,014	93.1	102,043
	Other	12,784	5,200	28.9	17,984
	Total:	51,968	110,225	68.0	162,193
Nonhalogenated solvents	F003	16,713	182,994	91.6	199,707
	F004	97	0	0	97
	F005	13,237	83,804	86.4	97,041
	Other	14,964	8,387	35.9	23,351
	Total	45,011	275,185	85.9	320,196
All solvents/ ignitables		123,119	422,074	77.4	545,193

Source: DPRA Analysis of the National Survey, Reference 26.

A breakdown of individual solvent types which are most frequently recycled is shown in Table 3.3.3, ranked in decreasing order of volume recycled. As shown, the surveys of solvent recyclers by the NASR[8] and the state of Illinois[11] show good agreement. The National Survey,[8] which reported the bulk of its solvent as RCRA F001 through F005, does not correspond as well with these other surveys or with solvent generation rankings (Table 3.2.3). Thus, it is judged to be a less accurate indicator of relative volumes of specific solvents recycled.

Table 3.3.4 summarizes the distribution of waste solvents recycled offsite by the previous use of the solvent. Wastes will be recycled primarily on the basis of net costs relative to other waste management alternatives. Although halogenated solvents have generally higher replacement costs relative to nonhalogenated solvents, the latter were recycled as frequently on a percentage basis. This results from the fact that nonhalogenated solvent wastes tend to be higher in solvent concentration,[31] 2.5[8] to 5.0[31] times larger in average waste stream volume and are more amenable for use as a fuel substitute. The National Survey data also show that off-spec commercial products are frequently recycled, despite small average stream volume, and low volume streams are more commonly recycled in offsite facilities.[8] These reflect the economics associated with ease of recycling and economies of scale, respectively.

Characteristics of recycled solvent and ignitable wastes have been summarized in Table 3.3.1. Wastes used as fuel or otherwise recovered tend to have high solvent concentrations, as would be expected. Nearly all wastes shipped to offsite recovery facilities are highly concentrated with solvents except for streams with other recoverable constituents (e.g., solvent contaminated oil). Recycling of wastewater and solids currently contributes little to total recycled solvent quantity.[18,31]

Table 3.3.5 summarizes characteristics of solvent wastes recycled offsite by previous use of the solvent. Vapor degreasing wastes tend to be low volume streams with high oil, low solids and high solvent contents. Conversely, dry cleaning solvent wastes are high in solids and water content.

TABLE 3.3.3. RELATIVE RANKING BY DEGREE OF RECYCLING

	NASR[1]	Illinois reprocessors[2]	National Survey[3]
Xylene	1	1	4
Toluene	2	2	6
Acetone	3	4	3
Methyl ethyl ketone	4-5	3	1
1,1,1-trichloroethane	4-5	5	2
Methylene chloride	6	7	5
Methanol	7-8	11	9
Perchloroethylene	7-8	9	8
Trichloroethylene	9-11	6	7
Methyl isobutyl ketone	9-11	10	10
Isobutanol	9-11	13	17-18
Freon	12	8	13
N-butyl alcohol	13-14	12	17-18
Cyclohexanone	13-14	-	-
Ethyl acetate	15-17	-	-
Ethyl benzene	15-17	-	-
Dichlorobenzene	15-17	-	-
Chlorobenzene	18-23	-	-
Carbon sulfide	18-23	-	-
Ethyl ether	18-23	-	-
Cresols	18-23	-	-
Nitrobenzene	18-23	-	-
Pyridine	18-23	-	-

[1] Source: Written communication between Emery Hukill, President of NASR and GCA, May 4, 1981, Reference 11.

[2] Source: Survey of Illinois Solvent Reprocessors. 1983, GCA, Reference 11.

[3] Source: Frequency reported in the National Survey for recycling in 1981. Engineering Science, Reference 8.

TABLE 3.3.4. DISTRIBUTION OF OFFSITE RECYCLED WASTE SOLVENTS BY PREVIOUS USE (%)

Previous use	Xylol	MEK	TCE	1,1,1-TCE	Toluol	Acetone	Methlene Chloride	PCE	MIBK	Methanol	Isobutanol	Butanol	Freon	Miscellaneous priority solvents	Potentially ignitable solvents
Wash Solvents	44.15	63.85	3.18	1.57	40.31	39.56	1.75	1.48	72.32	50.64	0.00	96.33	48.11	47.42	38.95
Metal Cleaning & Vapor Degreasing	0.00	0.00	64.98	70.23	0.00	0.00	11.17	8.59	0.00	1.45	0.00	0.00	2.76	4.24	1.97
Paint Solvent Waste	7.06	6.92	0.00	0.00	14.99	12.33	10.14	5.30	4.27	1.18	0.00	0.00	0.00	11.43	13.40
Dry Cleaning	0.00	0.00	0.00	0.93	0.00	0.06	0.31	15.61	0.00	2.60	0.00	0.00	4.31	0.00	0.15
Ink Solvent	0.13	0.76	0.00	0.00	0.48	0.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16
Off-spec Products	0.00	0.77	0.00	0.00	0.89	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
Heat Exchange	0.00	0.00	0.10	0.00	0.00	0.00	0.33	0.00	0.00	5.86	0.00	0.00	0.00	0.00	1.29
Other[a]	48.66	27.70	31.74	27.27	43.33	45.72	76.29	69.02	23.42	38.26	100.00	3.67	44.83	36.92	43.72

[a] Includes wastes categorized as thinners, blending solvents, and unspecified waste solvents.

Source: Adapted from GCA. Reference No.

TABLE 3.3.5. CHARACTERISTICS OF WASTE SOLVENTS RECOVERED OFFSITE

Previous use	Number of waste streams	Average waste stream volume (MT/YR)	Average waste composition (%)						
			Halogenated priority solvents	Nonhalogenated priority solvents	Potentially ignitable solvent	Water	Oil	Solids	Solvent
Wash Solvents	150	134	3.66	55.79	21.57	6.53	1.82	10.61	81.02
Vapor Degreasing & Metal Cleaning	112	31	85.28	1.43	4.75	0.06	8.17	0.31	91.46
Paint Solvent Waste	41	123	49.58	6.28	32.22	1.04	0.43	10.45	88.08
Dry Cleaning	4	71	53.85	1.75	4.79	11.13	0.0	28.49	60.39
Ink Solvent Waste	2	52	0.0	72.39	12.69	7.54	0.0	7.39	85.08
Off-spec Product	2	102	0.0	62.27	18.68	0.0	0.0	19.05	80.95
Heat Exchanges Waste	5	33	6.13	5.99	81.56	1.15	1.41	3.77	93.68
Other[a]	195	127	16.51	35.76	18.00	6.59	5.75	17.39	70.27

[a] Includes wastes categorized as thinners, blending solvents, or unspecified waste solvents.

Relative to solvent wastes managed through other treatment processes, recycled wastes frequently contain metals; e.g., Cr, Ni, Hg and Pb.[31] However, metals are found most often in halogenated wastes and rarely in wastes which are used as fuel supplements.[31] The latter also tend to have fewer solvent constituents relative to waste managed in other processes.

The primary end uses of recycled solvents and ignitables include use as a fuel, direct reuse as a feedstock and recovery for reuse. Onsite recycling practices, as summerized in the National Survey, are presented in Table 3.3.6. As shown, most solvent wastes are recycled as a reclaiment whereas ignitables are predominately used as fuel. Only 1 percent of recycled halogenated wastes are used as fuel versus 11 percent for nonhalogenated solvents. An independent survey of wastes burned as fuel performed by WESTAT in 1983 showed a similar distribution between these waste categories.[36] Nearly three-fourths of waste derived fuel was ignitables, one fourth was nonhalogenated solvents and less than 2 percent was halogenated solvents.

Finally, the ISDB[31] provided a further breakdown of recycling practices (excluding use as a fuel) for solvent wastes by residual category (Table 3.3.7). Major residual categories included distillation residues (51 percent) and light ends (38 percent). The majority of these residuals (78 percent) were recovered for sales, whereas reuse in a process accounted for the remaining 22 percent of known reuse methods. Use as a fuel was not identified by residual category. If this method of reuse is included, the distribution between handling methods becomes 66 percent reclaimed (i.e., for sales), 15 percent used as fuel, and 19 percent reused as a feedstock.[30] Use as a fuel accounted for only 0.2 percent of halogenated and 17 percent of nonhalogenated solvent recovery.

3.3.2 Incineration

Quantities of solvents and ignitables incinerated are summarized in Table 3.3.8 by management method as provided by the National Survey.[8] These represent maximum values, since the total quantity of wastes which reported

TABLE 3.3.6. ONSITE RECYCLING PRACTICES FOR SOLVENT AND IGNITABLE WASTES[a]

Recycling method	Percentage of onsite quantity recycled Halogenated Ignitables	 Nonhalogenated solvents	 Solvents	All solvent ignitable wastes
Recycled or reclaimed as a feedstock	22	1	5	10
Used as fuel or fuel supplement	49	1	11	24
Recycled in a manner constituting disposal	1	0	6	0
Recycled as a reclaiment	24	96	83	64
Other recycle	4	2	1	2

[a]Note: Total presented is a maximum value that includes double-counting of a small number of streams. Refer to Table 3.2.1 for actual totals.

Source: Engineering Science, Reference 8.

TABLE 3.3.7. RECOVERY PRACTICES FOR RCRA HAZARDOUS WASTES BY RESIDUAL CATEGORY (MT/YR)

Residual category	Unspecified recovery	Reuse in in same process	Reuse in in different process	Recovery for sales	Total recovery and reuse	Percent of residual volume undergoing recovery	Percent of all solvent recovery
Spent solvents	16,962	37,398	1,161	137	55,658	67.0	4.7
Distillation residues	62,222	210	23,122	513,636	599,190	78.9	50.8
Miscellaneous heavy ends	15,591	0	41,274	2,784	59,649	50.5	5.1
Condensible light ends	8,825	515	6,166	228,214	243,720	86.6	20.6
Noncondensible light ends	0	0	119,545	90,000	209,545	61.4	17.8
Off-specification products	307	7,619	4,318	500	12,744	4.5	1.1
Total Residuals	103,907	45,742	195,586	835,271	1,180,506	-	-
Percent of known recovery/reuse method	-	4.2	18.2	77.6	-	-	-

Source: Adapted from ISDB, Reference No. 31.

TABLE 3.3.8. TREATMENT OF SOLVENT AND IGNITABLE WASTES BY INCINERATION[1]

Treatment process	Waste category			
	Ignitables	Halogenated	Nonhalogenated	Total
Incineration only	40,140,456	46,205,850	34,149,611	120,495,917
Tank and incineration	47,140,000	7,910,000	69,841,463	124,891,463
Incineration and other	3,171	--	1,486,251	1,489,422
Tank and surface impoundment and incineration	6,134,147	--	--	6,134,147
Surface impoundment and incineration	408,049	--	100,488	508,537
Total:	93,825,823	54,115,850	105,577,813	253,519,486

Source: Engineering Science, Reference 8.

incineration along with other processes was included in this total. Relative to other wastes, a disproportionately high fraction of halogenated wastes are incinerated.[8,31]

Physical profiles of incinerated wastes were also provided.in the National Survey as summarized in Table 3.3.9. The major waste categories incinerated were organic liquids (59 percent), followed by inorganic liquids (37 percent). Very little solid or sludge (1.8 percent) was reportedly incinerated, possibly as a result of coding interpretations which categorized still bottoms and other slurries as organic liquids.[8] Typical incinerated wastes containing priority solvents tend to have low volume, high solvent content (Table 3.3.1), low frequency of occurrence of heavy metals and a low number of organic solvents per stream relative to solvents handled in other waste management methods.[31]

Finally, waste constituents incinerated have been reported by the Mitre Corporation as the result of a 1983 industry wide survey.[37] These data are presented in Table 3.3.10 in decreasing order by volume. These compounds include all the priority solvents affected by the land disposal ban. Halogenated compounds accounted for only 14 percent of the volume which suggests that they are present in lower concentrations or lower total waste volume. Both of these possibilities are supported by other data.[31]

3.3.3 Treatment Methods

Treatment methods summarized by ES were only provided for ignitable wastes, since solvent treatment data was judged to be insufficiently validated to provide useable information.[8] Table 3.3.11 summarizes the most commonly used treatment methods in tanks for ignitables by frequency of use. Physical separation methods accounted for 64 percent of treatment methods with chemical treatment practiced on 28 percent of the waste streams. Miscellaneous treatment processes accounted for the remaining 8 percent.

Land Disposal--

Solvent and ignitable wastes managed by land disposal are summarized in Table 3.3.12 by waste category and management practice.[18] Excluding two large waste streams which are managed through deep-well injection yields the

TABLE 3.3.9. PHYSICAL FORMS OF INCINERATED SOLVENTS AND IGNITABLES (GALLONS/YEAR)

	Physical							
Waste type	Solids	Inorganic sludges	Inorganic liquids	Organic liquids	Organic sludges	Miscellaneous	Unknown	Total
Ignitables	3,005,701	--	12,893,269	24,515,214	1,654,428	2,659,632	49,097,579	93,825,823
Halogenated solvents	--	--	39,878,053	13,491,806	590,976	--	155,015	54,115,850
Nonhalogenated solvents	210	--	21,793,585	82,087,571	347,497	746	1,348,210	105,577,819
Total:	3,005,911	--	74,564,907	120,094,591	2,592,901	2,660,378	50,600,804	253,519,492
Percent of known waste forms	1.5	0.0	36.7	59.2	1.3	1.3	0.0	100.0

Source: Engineering Science, Reference 8.

TABLE 3.3.10. PRIORITY SOLVENTS INCINERATED IN 1981

Constituent	Number of waste streams containing constituent	Amount of constituent incinerated (million gallons)
Methanol	95	44.4
n-Butyl alcohol	9	32.3
Toluene	10.3	17.3
Acetone	80	17.2
Xylene	78	15.2
Methyl ethyl ketone	54	14.0
Ethyl acetate	24	9.62
Tetrachloroethylene	19	6.74
Chlorobenzene	21	6.18
Cresols	8	5.92
Methylene chloride	26	5.84
1,1,1-Trichloroethane	23	5.05
Methyl isobutyl ketone	10	4.68
Isobutanol	9	4.50
Pyridine	9	4.38
Trichloroethylene	15	3.69
Carbon tetrachloride	9	0.547
Trichlorofluoromethane	2	0.401
Cyclohexanone	4	0.344
Ethylbenzene	6	0.264
Ethyl ether	2	0.248
1,2-Dichlorobenzene	2	0.240
Carbon disulfide	3	0.128
Nitrobenzene	3	0.0057
1,1,2-Trichloro - 1,2,2-Trichloro ethane	2	0.0008

Source: Mitre Corporation, Reference No. 37.

TABLE 3.3.11. MOST FREQUENTLY PRACTICED TREATMENT TECHNIQUES IN TANKS FOR IGNITABLE WASTES[1]

Technique	Frequency	Percent[1]
Physical methods		
1. Decanting	261	21.8
2. Sedimentation	180	15.0
3. Blending	172	14.4
4. Filtration	56	4.7
5. Clarification	27	2.2
6. Flotation	22	1.8
7. Solvent recovery	21	1.7
8. Other physical separation	21	1.7
9. Other physical removal	13	1.1
Subtotal:	773	64.4
Chemical methods		
1. Chemical oxidation	161	13.4
2. Neutralization	68	5.7
3. Chemical fixation	64	5.3
4. Chemical reduction	34	2.8
5. Activated carbon	13	1.1
Subtotal:	340	28.3

[1] Note= 7.3 percent of waste streams reported miscellaneous treatment methods.

Source: Engineering Science, Reference 8.

following distribution: deep-well injection - 43 percent, landfill - 42 percent, surface impoundment - 9 percent, and other - 7 percent.

Physical profiles of land disposed solvent and ignitable wastes were also provided in the National Survey.[8] The majority of solids and sludges are landfilled (75 percent) with the remainder disposed in surface impoundments (18 percent) and land applied (7 percent). Inorganic liquids account for only 0.4 percent of landfilled waste, thus the distribution between ignitables (25 percent), halogenated (52 percent), and nonhalogenated solvents (22 percent) provided in Table 3.3.12 is representative of actual constituent quantities disposed. In general, implementation of the solvent land disposal ban will have the most severe impact on generators of spent halogenated solvents. This data is supported by results obtained from the ISDB[31] which showed 84 percent of landfilled waste solvent volume containing halogenated solvents (versus 70 percent in the National Survey).[30]

As shown in Table 3.3.1, landfilled wastes tend to have higher solvent concentration (10.6 percent) and lower waste stream volume relative to solvent wastes handled in other waste management practices. They also tend to be more frequently contaminated with heavy metals, particularly Cr and Ni.[31] Wastes handled in tanks and impoundments tend to be very low in solvent concentration and contain multicomponent mixtures. These wastes have little potential for solvent recovery.

TABLE 3.3.12. QUANTITIES OF SOLVENT WASTE STREAMS CURRENTLY MANAGED BY LAND DISPOSAL[a] (MGY)

Management practice	Waste category			Total
	Ignitables	Halogenated	Nonhalogenated	
Deep well injection	14.2	290[b]	12.3	316.5[b]
Surface impoundment (disposal only)	5.3	6.1	0.9	12.3
Landfill	15.1	31.3	13.3	59.7
Land application	3.2	-	-	3.2
Surface impoundment and land application	5.3	-	-	5.3
Surface impoundment and landfill	-	0.8	0.9	1.7
Total:	43.1	328.2[b]	27.4	398.7[b]
Total after removal of two wastewater streams currently deep-well injected	43.1	73.2	27.4	143.7

[a] Note: These data gave been recently revised by the EPA (see Table 3.2.1). Therefore values presented here should only be used to provide an approximate distributuion of wastes between management practices.

[b] Estimates include two wastewater streams totalling 255 million gallons.

Source: Engineering Science, Reference 8.

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SECTION 4.0

COMMERCIAL OFFSITE RECYCLING, TREATMENT, AND DISPOSAL CAPACITY

This section summarizes commercial recycling, treatment, and disposal capacity available for handling solvent wastes which are scheduled to be banned from land disposal. The commercial solvent recycling industry is discussed to provide insight into its processing capabilities and current practices. This is followed by a summary of available data on recycling, incineration, and waste fuel burning capacity. These represent the bulk of available land disposal alternatives for nonaqueous wastes.

4.1 COMMERCIAL SOLVENT RECYCLING INDUSTRY

The current commercial solvent recycling industry consists of at least 135 firms with 243 facilities nationwide.[1] Of these, 13 percent accept only halogenated solvents and 6 percent accept only nonhalogenated solvents. The latter tend to be waste oil dealers and fuel blenders, while the former are generally chemical distributers, equipment vendors (e.g., degreasers), or small firms which only process expensive solvents due to economic considerations. Overall, approximately 25 to 30 percent of the solvents handled are halogenated (see Section 3.3.1). The solvent reclaiming industry is represented by the National Association of Solvent Recyclers (NASR) which is comprised of 43 solvent reclaiming firms, accounting for approximately 70 percent of offsite recycling capacity.[2]

Large firms tend to serve regional markets and are capable of producing high-purity solvents through the use of distillation, fractionation, and other specialized recovery techniques. Their market edge is enhanced by laboratory facilities, skilled operators, and a good understanding of regulations. These firms are often involved in other hazardous waste operations (e.g., transportation, treatment, storage, or disposal facilities) and represent approximately 3 percent of the solvent reclaiming facilities.[3]

Small firms, representing approximately 70 percent of the solvent reclaiming facilities, have limited recycling capabilities.[3] Roughly half of these facilities operate small distillation units while the remainder rely on filtration, precipitation and decanting to recover or blend solvents for use as fuel supplements.[3] Medium-sized firms exhibit capabilities ranging between those of the other size classes, but they lack the distribution networks of the large firms.

Several sources of information regarding the solvent recycling industry have been identified which provide information on the types of wastes handled, treatment processes employed, costs, capacity utilization, and residual handling practices.

GCA and Metcalf & Eddy (M&E) surveyed and profiled 22 recycling firms in 1985 for the EPA's Office of Research and Development.[4] An earlier survey was performed by the NASR in 1982, which resulted in 31 telephone responses from its member firms.[2] Finally, the State of California Department of Public Health performed a statewide survey of solvent reclaiming operations in 1984, identifying 11 facilities.[5] Data generated from these surveys on processing capabilities and residual handling practices are summarized in Table 4.1.1. The GCA and NASR surveys targeted larger facilities which represent the bulk of solvent management capacity, particularly for wastes which are less easily recycled.

Several conclusions from these surveys can be drawn:

- The use of some form of distillation is universal among larger firms. The only facilities without some type of evaporative or distillation technology were a blending facility and a facility using destructive wet air oxidation;
- A majority of the facilities (70 percent) use bottom residuals (particularly nonhalogenated) as fuel and restrict processing to maintain a pumpable liquid;
- Recovery ranged from 74 to 98 percent at the four sites which reported data; and
- Drying recovered solvents is fairly common although this practice, like decanting and filtration, was rarely reported in the NASR survey.

TABLE 4.1.1. SUMMARY OF COMMERCIAL SOLVENT RECYCLING SURVEYS

	Number of facilities using process					
Process type	California survey[1]	GCA/M&E survey[2]	NASR survey[3]	Total facilities using process	Percent of facilities using process	Comments
Simple distillation	11	22	11	44	61	Three flash units. Seven vacuum units. Some equipment with surge columns.
Fractionation (including packed column)	3	14	5	22	31	
Thin-film evaporation	5	25	13	43	60	Of nine specified, five were vacuum.
Steam stripping	5	6	7	18	25	
Drying	9	2	6	17	24	Seven molecular sieve, five calcium chloride, and one each for caustic extraction, ionic resin, and drum dryer.
Solvent extraction	0	4	2	6	8	
Use as fuel	5	14	29	48	67	Of 30 which specified use: 67% cement kiln, 16% boilers, 17% steel furnaces.
Landfill	6	NA	23	29	58	
Incineration	0	NA	10	10	20	
Total facilities in survey	11	22	39	72	-	

[1] Source: State of California Survey, Reference 5.

[2] Source: GCA/Metcalf & Eddy Survey, Reference 4.

[3] Source: Engineering Science/NASR Survey, Reference 2.

Wastes exhibiting certain characteristics are sometimes not accepted by recyclers, including:

- Low flash point materials - wastes with a flash point of less than 100°F.
- High solids content wastes - solids contents of 30 to 50 percent (60 percent for steam injection) are limiting values reported by reclaimers. Others specify minimum recoverable solvent levels of 50 to 60 percent.[6,7] However, one facility was identified which ground high solid wastes to ≤800 μm, and suspended this waste in a solvent/oil blend for use as a fuel.[4]
- Heavy metals and cyanides were also restricted at some facilities, but concentration limits were not provided.

Other restrictions adopted by some solvent reclaimers include minimum waste volumes and requirements that the recovered, and sometimes, the residual bottoms product are returned to the supplier.

Wastes accepted for recycling tend to be highly concentrated with solvents. Analysis of waste characterization data provided by Illinois reprocessors showed two-thirds of the total waste quantity recycled contained over 70 percent solvent.[8] Less than 3 percent contained 10 percent or less solvent and 41 percent contained over 90 percent solvent (see Figure 4.1.1).[8] Wastes with very low solvent content (less than 30 percent) tended to be wastewater washes and line rinses. Wastes with solvent contents ranging from 30 to 60 percent were dominated by oily wastes such as degreasing solvent distillation residues. Highly concentrated wastes were contaminated solvents which were not recovered to a significant extent by the generators.

Solvent recovery rates reported in the literature average around 75 percent[5,6,7] with values ranging from less than 60 percent[5] to 99 percent.[9] Safety Kleen, which recovered 23.6 million gallons of spent parts cleaning solvent (D001) in 1982, reported average recovery rates of 92 percent with an additional 7 percent being blended as fuel. However, spent chlorinated immersion cleaning solvent recovery averaged only 74 percent.[9]

The extent of solvent recovery is determined either by equipment processing capability or constraints imposed by the end-use of the bottoms product. The NASR survey showed that at least 62 percent of solvent bottoms from commercial recovery facilities are used as supplemental fuel.[2] These

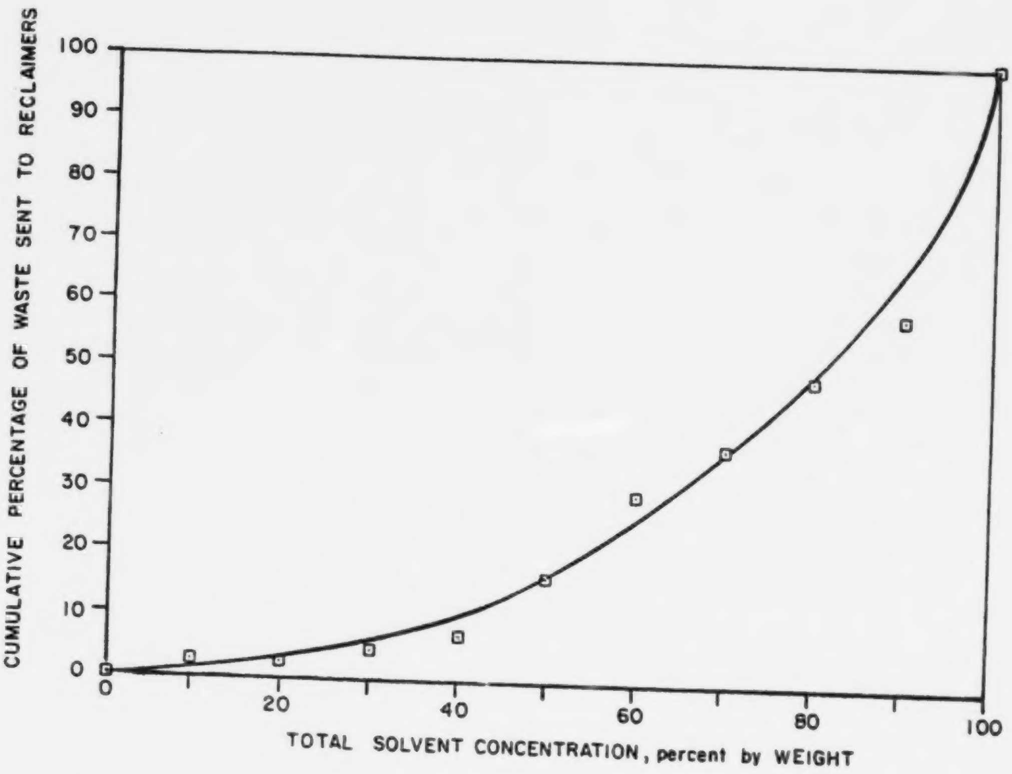

Figure 4.1.1. Solvent wastes recycled by commercial reprocessors in Illinois.

Source: Reference No. 8.

materials are deliberately kept in a pumpable state for ease in handling, as are wastes which are treated through liquid injection incineration. Restrictions on wastes accepted for use as a fuel blend include maximum solids content (30 to 50 percent maximum) and chlorine content (0 to 10 percent after blending with typical limits of 3 to 5 percent). One case was identified where chlorine contents of up to 35 percent were accepted for a kiln producing low alkali cement.[4]

Solvent bottoms destined for rotary kiln incineration or landfills, in particular halogenated solvents, are processed to the extent allowable in the facility's recovery equipment. Simple coil-still distillation units are least able to process high solids wastes, whereas steam injection stills and thin-film evaporators can operate at higher solids levels (see Section 7.0). Certain distillation recovery units with lined boilers have been reported to reduce solvent concentrations in the bottoms product to less than 1 percent.[10] One facility used a double-drum dryer to reduce nonflammable solvent bottoms to 99.9 percent solid.[4] In the literature, facilities were reported to add nonvolatile liquid additives to distillation units to keep bottoms in a fluid state as solvent is recovered.[6]

Other uses for chlorinated bottoms products that have been reported include use as an asphalt extender and incorporation into a building product (concrete block extender).[8]

Commercial Recycling Costs--

Commercial solvent recycling costs are summarized in Table 4.1.2. Toll arrangement costs typically vary from $0.20 to $1.70/gallon. Sell-back prices are 70 to 90 percent of virgin product prices, whereas open-market sales range from 50 to 90 percent. These are lower due to increased uncertainty regarding the presence of undesirable contaminants. Disposal costs in cement kilns and light aggregate manufacturers range from revenue of $0.05 to a cost of $0.35/gallon[5,7,11] with an average cost of approximately $0.20/gallon. Incineration costs are highly dependent on physical form of the waste, but typically range from $0.30 to $1.25/gallon for liquids and $1.30 to $4.20 for solids.[11] More details on costs are provided in Sections 7.0 through 12.0 for specific technologies.

TABLE 4.1.2. COST FOR SOLVENT RECOVERY AT COMMERCIAL FACILITIES

Source (Ref. No.)	Year	Percent solid	Toll arrangement ($/gallon)	Sell-back arrangement (% of virgin price)	Open market (% of virgin price)
3	1983	5	0.60	80 - 90	50 - 90
		10	0.80		
		15	1.10		
		20	1.70		
5	1984		0.75		
13	1983		0.15 - 1.50		
6	1976		0.20 - 10.00	80 - 90	50 - 90
8	1982				65
7	1982		0.50 - 1.00 (0.70 average)		
5	1984		0.75 - 1.60		
11	1984		0.10 - 1.55		
4	1985		0.40 - 1.55	80 - 90	
12				70 - 80	

Costs for offsite reprocessing of solvents vary as a function of the waste volume, percent recycleable material (including solvent, metals, oil, etc.), disposal method required for the residuals, transportation mode and distance, and the selling/purchasing arrangement. In "toll" arrangements, solvents are typically segregated, recycled in a batch mode, and returned to the generator for a fee based on the recycler's internal costs and profit margin. Sell-back and open-market arrangements involve purchase of solvents from generators at a nominal fee and sale of reprocessed solvent. Sales price is some fraction of the market value of virgin material which is dependent on product purity and other factors. Toll arrangements are common among generators using solvent blends in applications which can tolerate some degree of contamination. Conversely, open-market arrangements are used by firms such as electronics manufacturers which prefer to purchase virgin product.

Transportation costs vary most directly with distance, but also with mode of transport (e.g., ship, rail, truck), containment method (e.g., tank, drum, bulk), special shipping requirements (e.g., ignitable wastes, manifests), and waste volume. Typical one-way transportation costs by truck are summarized in Table 4.1.3.

TABLE 4.1.3. WASTE SOLVENT TRANSPORTATION COSTS
(COSTS = ¢/GALLON/MILE)

Source (Ref. No.)	Year	Drum	Bulk	Not specified
3	1983	0.09 - 0.13	0.07 - 0.10	-
13	1983	0.06 - 0.010	-	-
11	1984	-	-	0.06 - 0.08

4.2 AVAILABLE RECYCLING TREATMENT AND DISPOSAL CAPACITY

In order to establish effective dates for enactment of the land disposal ban, the EPA was required to assess available alternative recycling, treatment and disposal capacity. The results of this analysis were presented with the January 14, 1986 proposed rule for the land disposal restrictions[14] as summarized below.

The EPA assumed 1,202 million gallons/year (MGY) of solvent wastes currently land disposed would be subject to the land disposal provisions. This excludes wastes which are currently deep-well injected (exempt from regulation until August 8, 1988), but includes wastes which are treated or stored in impoundments. EPA evaluated the economic feasibility of impoundments meeting the regulatory requirements which permit them to continue operating under the ban (RCRA Section 3005(j)(11)(A) and (B)). Based on this analysis, EPA determined that 80 percent of the volume currently treated will meet the exemption requirements leaving 185 MGY requiring alternative treatment. The remaining waste which will require alternative treatment or recycling capacity is 20.6 MGY of organic liquid, 10.4 MGY organic sludges and solids, and 6.7 MGY of inorganic sludges and solids as summarized in Table 4.2.1.

TABLE 4.2.1. SOLVENT WASTE QUANTITY REQUIRING ALTERNATIVE TREATMENT (MGY)

Solvent waste type	Currently land disposed	Small quantity generators	Still bottoms from recovery of banned organic liquid	Total
Inorganic aqueous wastes	185.0	-	-	185.0
Inorganic sludges and solids	6.7	-	-	6.7
Organic liquids	14.6	6.0	-	20.6
Organic sludges and solids	7.3	1.9	1.2	10.4
Total:	213.6	7.9	1.2	222.7

Source: U.S. EPA, Reference 14.

The EPA assumed all aqueous wastes would undergo some form of wastewater treatment. Fifty percent of halogenated and one-third of nonhalogenated liquids would undergo some form of distillation generating 1.2 MGY of still bottoms (14 percent of original waste volume). These bottoms and the remaining waste would undergo incineration. Use as a fuel was not considered as an available alternative disposal practice due to uncertainty regarding the impact of waste-derived fuel regulations which are currently being developed. Also, due to lack of capacity data, other treatment options were not considered.

EPA assumed all wastes would require offsite recycling, treatment or disposal due to lack of information on available capacity at solvent waste generators. Unused offsite distillation capacity was taken from the NASR survey (224 MGY)[2] and tank capacity for treating wastewater was derived from the National Survey (112 MGY).[15] Incineration capacity was estimated to be 25.6 MGY, based on design capacity data and an assumed current utilization rate of 80 percent.[14]

Capacity requirements and unused capacity data are summarized in Table 4.2.2. As shown, there is not sufficient commercial capacity to incinerate inorganic sludges and solids or to treat aqueous wastes. Thus, EPA proposed a 2-year extension of the land disposal ban for these materials to ensure that sufficient capacity will be available.

It is possible that the quantity of recoverable solvent in wastes which are currently land disposed is less than that estimated by EPA. EPA assumed 42 percent of currently land-disposed organic liquids would be recoverable, yielding a bottoms product of only 14 percent of the original waste volume. Analysis of waste characterization data[16] shows only 37 percent of landfilled waste with a total solvent concentration exceeding 10 percent by weight. Concentrations ranged from near 0 to 36 percent total solvents with a volume weighted mean of 11 percent. Thus, even if all the solvent could be recovered, the bottoms product would be nearly 90 percent of the original waste volume. If these data are assumed to accurately represent landfilled solvent wastes, the resulting incineration demand would become 28.7 MGY, which exceeds available capacity by more than 3 MGY. Other

TABLE 4.2.2. ANNUAL TREATMENT AND RECOVERY CAPACITY DEMAND AND AVAILABILITY (MILLION GALLONS/YEAR)

Inorganic wastes	Wastewater treatment	Distillation	Incineration of organics	Incineration of inorganics
Inorganic wastes:				
Solvent-water mixtures	185			
Sludges and solids				6.7
Organic wastes:				
Halogenated liquids		5.4	5.5	
Nonhalogenated liquids		3.2	6.5	
Halogenated sludges and solids			7.2	
Nonhalogenated sludges and solids			3.2	
Total capacity demand	185	8.6	22.4	6.7
Available capacity	112	225	25.6	0
Capacity shortfall	73	0	0	6.7

Source: U.S. EPA, Reference 14.

studies[5,12] show higher fractions of recoverable solvent in land disposed waste but, with current recovery practices, the bottoms product would still represent closer to 50 percent of the original waste volume.

Additional factors which should be considered include the geographical distribution of available capacity and the physical form of the waste. WESTAT indicated that four out of the ten EPA regions have severely restricted commercial treatment capacity.[15] Also, much of the required capacity is going to be needed to incinerate solids and sludges. This will put further strains on available local capacity, since these types of equipment (e.g., rotary kilns, fixed hearth) represent a modest fraction (20 percent) of total hazardous waste incinerators in the country.[17]

Capacity for liquid wastes is expected to be less of a problem since more wastes are ammenable to recovery and alternative treatment practices.[11] However, overall capacity utilization at commercial facilities may exceed the 80 percent figure used in EPA's determination of available capacity, and demand could increase in the short-term if boiler regulations force burners of waste-derived fuel to find alternative disposal methods.[11]

Finally, it is unclear how waste solvent land disposal quantities have changed since 1981. Overall, landfilled waste quantity has increased 40 percent from 1981 to 1984 at eight facilities which, in 1981, accounted for 80 percent of the landfill market.[11] However, this growth rate has been outpaced by resource recovery and incineration[11] which, combined with low growth in solvent demand,[1,3] suggests that land disposed solvent quantities have increased modestly at best.

Despite the above considerations, a capacity shortage is not likely to result for two primary reasons. First, the quantity of waste requiring alternative means of disposal is likely to decline in response to the land disposal ban. Increased waste minimization and use of technologies yielding higher solvent recovery rates will be implemented as the next lowest cost alternative to land disposal. These practices will essentially be forced, since there is currently no economical, commercially demonstrated, means to solidify or encapsulate wastes containing large quantities of solvent which do not result in significant releases through leachate generation. Secondly, required incineration capacity is also likely to be lower since other treatment and disposal alternatives will be utilized; e.g., use as fuel, wet air oxidation, etc. These factors are discussed below.

Increased product and process substitution and other waste minimization activities are likely to reduce solvent demand and waste generation. Waste segregation may result in lower volumes of waste solvents, particularly for aqueous wastes. Availability of small-scale, high-recovery package distillation units should significantly reduce solvent waste generation from small-quantity generators (21 percent of nonaqueous solvent disposal capacity requirements). Finally, use of sludge driers or addition of oil or other nonvolatile liquids to still bottoms will enable recyclers to maximize solvent recovery and minimize the volume of waste requiring disposal. These methods are already in use, primarily for low Btu materials. They should become much more widely applied for all solvents when land disposal of the bottoms product is no longer an acceptable option.

Required commercial incineration capacity will also be lower as a result of other, more economical disposal options and available onsite incineration capacity. Data show that 90 percent[19] to 95 percent[2] of incinerated hazardous solvent wastes are handled onsite in units with low average capacity utilization (20 to 60 percent).[19] Since onsite incinerators tend to be operated by large firms, it is highly likely that a significant fraction of the organic liquids currently landfilled will be incinerated onsite when the cost advantage of landfilling is removed.

It is also likely that much of the estimated 186 MGY of hazardous waste currently used as fuel[20] will continue to be disposed in this manner due to the economic benefits resulting from utilization of its heating value. The distribution of this waste will shift towards more efficient, high temperature thermal processes (DRE's $\geq$99.99 percent) as a result of the impending EPA regulations. However, several types of high temperature industrial processing units have demonstrated acceptable destruction capabilities (see Section 12) and will be available for use. Due to reduced cost advantages of offsite versus onsite use as a fuel, increased onsite recycling of these solvent wastes is likely to occur to reduce the total volume requiring alternative disposal.

Use of halogenated wastes as cement kiln fuel blends is gaining increased popularity. In California, the quantity of halogenated wastes used as cement kiln fuel exceeds the quantity incinerated by a factor of 4.5.[5] One source estimated that the wet kiln capacity in the United States is sufficient to destroy nearly four times the annual quantity of chlorinated hazardous waste produced.[12] Cement kilns can use from 0.7 percent[5] to 1.25 percent[3] of their design feed as chlorine waste. Upon implementation of the land disposal ban, it is likely that solvent recovery operations will adopt methods to recover higher percentages of halogenated solvents. This will make these wastes more economically blended with spent nonhalogenated solvents and oils to attain the low chlorine content required for supplemental fuels.

Blast furnaces have also demonstrated acceptable DREs for halogenated wastes and are currently in use for destroying spent solvent wastes. For example, nine solvent reprocessors produce 30 MGY of recycled solvent waste bottoms (Cadence Product 312) which are sold to steel mill blast furnaces. The chlorine generated from burning the waste is said to prevent alkalis from building up on the furnace walls. Company officials say demand for the product is such that they could turn most of the solvent waste in the country into fuel for blast furnaces.[21]

Industries and thermal processes considered to be capable of yielding 99.99 percent DREs for nonhalogenated waste solvents include melting furnaces in the glass industry, blast and open-hearth furnaces in the iron and steel industry, rotary kilns in lime production, and [illegible]erbatory furnaces in the copper industry (see Section 12.0). Finally, [illegible]cesses such as wet air oxidation, super-critical fluids and others (see Sections 7.0 through 12.0) are gaining acceptance as cost-effective alternative treatment methods.

The EPA Office of Solid Waste is currently performing an analysis of recycling, treatment and disposal capacity utilization to support development of the land disposal ban provisions. The capacity determination is based on survey data being collected by the Office of Policy Assessment for both onsite and offsite TSD facilities and solvent reclaimers. Preliminary screening results, available in June 1986, are expected to form the basis for a detailed questionnaire. These data will be available by December 1986 and should provide valuable insight into both onsite and offsite recycling, treatment, and disposal capacity utilization.[22]

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SECTION 5.0

WASTE MINIMIZATION PROCESSES AND PRACTICES

Waste minimization, as defined here, consists of two distinct aspects of hazardous waste management: source reduction and recycling/reuse. Source reduction refers to preventive measures taken to reduce the volume or toxicity of hazardous waste generated at a facility; recycling/reuse refers to procedures and processes aimed at the recovery of generated waste or its reuse, e.g., as a fuel. The two approaches will be discussed separately in this section, using case studies to illustrate the potential of these activities for the control of hazardous solvent waste. However, as will become apparent from subsequent discussions, both source reduction and recycling/reuse are practices that often are carried out simultaneously by a facility, as management undertakes multifaceted programs to achieve waste minimization.

5.1 SOURCE REDUCTION

Source reduction is defined as any onsite activity which reduces the volume and/or hazard of waste generated at a facility. Source reduction represents a preventive approach to hazardous waste management, since the reduction of waste volume or hazard reduces problems associated with waste handling, treatment, disposal, or liability. Source reduction practices may impact all aspects of industrial processes generating hazardous wastes, from raw materials to equipment, to products. A primary motivation for plants to implement certain source reduction practices is the potential economic benefit they may accrue. These economic benefits increase as restrictions on waste management practices become more stringent.

Waste source reduction practices will vary widely from plant to plant, reflecting the variability of industrial processes producing wastes, and of the characteristics of the wastes themselves. In general, source reduction practices may be classified as follows:

- Raw material substitution;
- Product reformulation;
- Process redesign/modernization; and
- Waste segregation.

A brief description of each type of practice is presented below.

5.1.1 Raw Material Substitution

Raw material substitution involves the replacement of one feedstock, catalyst, or other material involved in production for another. The substitute is less hazardous or results in lower hazardous waste generation, while serving a similar function in the production process and satisfying the specifications of the end-product.[1] The ideal raw material substitution would be the replacement of a hazardous material with a nonhazardous material, while achieving equivalent product quality. The experience described in the literature, however, indicates that either some compromise in product quality, or some alteration in process equipment, is often required. Examples of raw material substitution include the use of water-based material in place of solvent-based materials (e.g., using an alkaline cleaner, instead of a solvent cleaner) and the use of prepared materials which eliminate the need for a hazardous material (e.g., using precoated metal parts thereby eliminating the need for solvent-based surface preparations). Aside from recycling, raw material substitution appears to be the most common source reduction practice employed in industry.

5.1.2 Product Reformulation

Another method that is employed to reduce the volume or toxicity of wastes produced by a plant is to change the product in some manner. This may involve the lowering or altering of certain product specifications (e.g., purity), changing the chemical composition, or changing the physical state. An example of product reformulation is shifting paint and coatings compositions to higher solids content resulting in a corresponding decrease in solvent content of rinses and off-specification product wastes. Product reformulation is considered relatively common in industry, particularly among manufacturers of specialty chemicals.[2]

5.1.3 Process Redesign/Equipment Modification

Process redesign includes the alteration of the existing process design to include new unit operations, the implementation of new technologies to replace older operations, changes in operating conditions employed in processing, or changes in operating practices affecting the process; e.g., housekeeping or maintenance. Process redesign can, therefore, vary widely in terms of the effect upon production, product quality, and operating expenses. Redesigning is often necessary when increasingly stringent environmental protection standards are to be met. Many processes which utilize solvents and produce solvent wastes appear to have been designed in an era when pollution control was not a priority.[3]

Equipment modification or modernization appears to be a prevalent method for achieving source reduction, despite the potentially high initial costs involved. New or better equipment may achieve the goals of source reduction in three ways. First, it may allow for the elimination of a hazardous material by performing mechanically an equivalent operation to a chemical process. An example of this may be the replacement of solvent cleaning of surfaces with a mechanical cleaning system. Second, new equipment may allow for the replacement of a hazardous material by a less hazardous one. For example, the use of high pressure alkali cleaning can replace solvent cleaning of equipment in the paint industry. Third, new or better process equipment may simply provide better environmental control. An example of this would be the installation of air pollution equipment such as a wet scrubber to collect organic vapors.

Improving process controls is considered a particularly important aspect of equipment modification. Process controls may be less costly and more technically feasible to implement than replacement or modification of large-scale equipment. Process controls include manual, automatic, and computer-controlled systems. Examples of the use of improved process controls in industry to reduce waste generation include the increased usage of computerized controls for paint formulation and batch dyeing operations in the textile industry. These operations often process a wide variety of raw materials.[3] Improved process control minimizes the potential for generating off-specification products and excess formulations which may otherwise be disposed.

The manner in which a process is operated may also be changed to effect waste reduction. This may be accomplished through the use of different temperatures or flow rates, by reducing the frequency of process startups or shutdowns, or by changing maintenance schedules. Improved housekeeping practices are commonly employed to achieve source reductions. These practices include minimizing equipment cleaning and maintenance, shutting down ancillary equipment when not in use, replacing gaskets, tightening valves, and other measures. Another manner in which process changes can effect source reductions is through increased management attention to pollution control and waste generation. For example, many companies offer employee incentive programs for identifying cost-cutting measures, some of which involve source reduction of solvent wastes.

5.1.4 Waste Segregation

Waste segregation entails special storage or handling procedures to avoid the mixing of different waste streams. The segregation of wastes allows for certain streams to be treated, recovered or reused, or disposed of in a more environmentally and perhaps economically sound manner. Segregation is particularly desirable in eliminating the mixing of toxic waste streams with nontoxic streams, which results in a larger volume of waste requiring management. Waste segregation most often will require implementation of new equipment to collect the separated streams. The technical and economic feasibility of waste segregation, therefore, may be somewhat limited. An example of waste segregation is the installation of settling systems to produce slurried or sludge wastes.

5.1.5 Case Summaries - Source Reduction

Numerous examples of source reduction practices have been documented in the literature. The industries involved in these practices are extremely diverse, ranging from large chemical manufacturing plants to small sized printing operations. Reduction of solvent hazardous wastes has been documented more often than any other type of waste. This is probably attributable to the multiple non-consumptive uses which solvents serve in industry and the favorable economics of recovery. A number of the documented cases of source reduction for solvents are discussed below and summarized in Table 5.1. The case studies are grouped in accordance with the source reduction practice which resulted in the most significant waste minimization. However, as noted in Table 5.1 and in the subsequent discussions, use of multiple minimization practices is not uncommon.

Raw Material Substitution--

Case No. 1: Rexham Corporation, Greensboro, N.C.--Rexham Corporation is a printer of product labels. Their primary waste stream is derived from an alcohol/acetate-based ink used in the flexographic printing process. The company substituted a water borne ink for several of their applications. The substitution reduced both waste solvent volume and solvent air emissions, with only a small effect upon their overall operations. The costs saved were not estimated.[4]

Case No. 2: Riker Laboratories, Northridge, CA--Riker Laboratories is a coater of medicine tablets. They had previously used a solvent-based coating solution. Because new air pollution standards would have required implementation of equipment totaling $180,000 to control solvent air emissions, the company replaced the solvent coatings with a new water-based material. This also required new process equipment and operating procedures. The substitution resulted in a reduction of 24 tons of waste/year, and a raw materials cost savings of $15,000/year.[1]

TABLE 5.1. SUMMARY OF WASTE REDUCTION CASES

Case number	Reference	Company	Industry/process type	Source reduction procedure	Recycling procedure	Cost savings	Comments
1	4	Rexham Corporation, Greensboro, NC	Printing and coating	Raw material substitution	Distillation	Raw material costs decreased by 16% ($5,000/yr) Waste disposal costs decreased by 74% ($22,800/yr) Payback of 1 yr	
2	1	Riker Laboratories, Northridge, CA	Coater of medicine tablets	Raw material substitution Equipment modification		Materials costs - $15,000/yr	Saved $180,000 in pollution control equipment that would have been required
3	1	Scovill, Clinton, NC	Manufacturer of electrical appliances	Raw material substitution	Reuse of solvents	Materials costs-$12,000/yr from the substitution, $5,320/yr from recycling Disposal costs-$3,040/yr	
4	1	Emerson Electric Co., Murphy, NC	Manufacturer of stationary power tools, metal finishing and painting	Equipment replacement Raw material substitution Managment improvement		Materials costs-$600,000/yr Disposal costs-$10,000/yr Labor costs-savings of 40% Managment system saved $147,000/yr	
5	1	3M Microelectronics, Columbia, MO	Manufacturer of flexible circuits	Equipment modernization Raw material substitution		Total savings of $15,000/yr	

(continued)

TABLE 5.1. (continued)

Case number	Reference	Company	Industry/process type	Source reduction procedure	Recycling procedure	Cost savings	Comments
6	4	Torrington Company, Walhalla, SC	Manufacturer of automobile bearings	Equipment replacement Raw material substitution		Expected payback period of 1 year	
7	4	Kemp Furniture Industries, Goldsboro, NC	Manufacturer of furniture products, coating operations	Equipment modernization Raw material substitution		Material cost savings of 23%/yr Payback period of 1 year	
8	4	ITT Telecom, Raleigh, NC	Manufacturer of telecommunications equipment, printed circuit boards	Process modification			
9	1	ICI Americas, Inc., Goldsboro, NC	Research on agricultural chemicals	Improved housekeeping		Total cost savings of $37,000/year	
10	1	Rexham Corporation, Matthews, NC	Printer and coater	Waste segregation	Reuse of solvents in equipment cleaning	Material reuse was almost 100% for solvents	
11	1	DeSoto Corporation, Greensboro, NC	Manufacturer of trade sales paints	Waste segregation	Reuse of solvent for paint formulations	Waste reduction of 98%	
12	1	Daly-Herring, Kingston, NC	Manufacturer of pesticides	Some recycled for processing, others sold for reuse	Materials costs-$2,000/yr Disposal costs-$9,000/yr		

Case No. 3: Scovill, Clinton, N.C.--Scovill manufactures small electrical appliances. The plant had previously used 1,1,1-trichloroethane (TCE) as a solvent degreaser. A water-based compound was substituted for the TCE for most of their applications, providing a cost savings of $12,000/year for raw materials. The company also began substituting waste solvents for virgin solvents in metal cleaning operations. The reuse of solvents resulted in an additional $5,320/year saving in material costs. Total costs of disposal that were saved as a result of these substitutions was $3,040/year, resulting in a net cost savings of $20,360/year.[1]

Other Cases--A large metal-working facility eliminated the use of cutting oils by replacing them with synthetic or water soluble machining lubricants and coolants. No information detailing cost savings was provided for this case.[4]

Process Redesign/Equipment Modification--

Case No. 4: Emerson Electric Company, Murphy, N.C.--Emerson Electric Company manufactures stationary power tools, which require both metal finishing and painting. Emerson substituted a water-based anodic electrostatic immersion paint system for an existing organic solvent paint system. This has resulted in increased productivity and product quality. The water-based system allows for recovery and reuse of paint. The resultant cost savings have been $600,000/year for paint, and nearly $10,000/year for disposal. Labor costs were decreased by 40 percent. In addition, air emissions and workplace exposure to solvents has been eliminated.[1]

Case No. 5: 3M/Microelectronics Division, Columbia, MO--The 3M's Microelectronics Division makes flexible electronic circuits from copper sheeting. Metal cleaning operations were previously performed using a chemical spray system. A new process has been installed which cleans the sheets mechanically instead of chemically, through use of a rotating brush system. The process resulted in a reduction of 40,000 pounds of waste/year. Raw materials, disposal, and labor costs were reduced by $15,000/year.[1]

Case No. 6: Torrington Company, Walhall, S.C.--Torrington Company manufactures bearings for the automobile industry. The bearings have a layer of oil coating on the metal surface to protect it from the stamping press. Later, heat treatment with oils is carried out. Torrington had previously used a 1,1,1-trichloroethane vapor degreaser to remove the stamping and quenching oils. The degreaser has been replaced with a new parts washer which uses hot water and a low cost alkaline cleaner. The installed parts washer cost was $40,000 and the company expected a payback period of one year. The new equipment reportedly reduced raw material costs significantly, and is considered to offer an improvement in worker safety.[4]

Case No. 7: Kemp Furniture Industries, Goldsboro, N.C.--Kemp Furniture Industries manufactures furniture products from particle board, press board, and plywood. Major operations involving solvents at the plant include the printing of wood grains and surface coating applications. A change in the spray guns used at their 25 coating booth from conventional air guns to air-assisted (airless) spray guns resulted in a materials savings of 23 percent. The payback period was estimated at one year.[4]

Case No. 8: ITT Telecon, Raleigh, N.C.--ITT Telecon manufactures telecommunication equipment using printed circuit boards (PCB). The plant had been using 1,1,1-trichloroethane as a developing agent, and methylene chloride as a stripping agent. ITT changed their process to permit use of an aqueous "photo resist" formulation. This allowed them to eliminate certain systems including distillation equipment, various emission controls, and vapor recovery units. The wastes generated were nonhazardous and could be disposed of in POTW sewers. Cost savings information was not provided for this case.[4]

Case No. 9: ICI Americas, Inc., Goldsboro, N.C.--ICI Americas, Inc. is involved in research on agricultural chemicals. They generate small quantities of a variety of wastes, including spent solvents. Housekeeping practices were implemented at the facility including separation of container facilities, identification of chlorinated and nonchlorinated solvents, and general maintenance. The company reports a 70 percent reduction in waste generation, and estimates a total cost savings of $37,000/year (based on 1984 dollars).[1]

Other Cases: Centrifuging--Spent solvent usage from degreasing may be reduced by centrifuging oily parts before degreasing. This practice is used by many companies. In some cases, centrifuge processes can be combined with a detergent spray to eliminate solvent degreasing altogether.[4]

Waste Segregation--

Case No. 10: Rexham Corporation, Matthews, N.C.--Rexham Corporation operates a coating facility in which a very large number of different chemical formulations are employed. A primary means of waste reduction implemented at the plant was the segregation of spent toluene solvent. This permitted the reuse, recovery, and sale of toluene, methyl ethyl ketone and incinerable solvents. Segregation allowed for almost 100 percent reuse of liquid toluene. Information detailing raw material cost savings was not provided.[1]

Case No. 11: DeSoto Corporation, Greensboro, N.C.--DeSoto Corporation manufactures trade sales paints. Waste mineral spirits are now collected in drums and set aside for reuse as a solvent. A waste reduction of 98 percent (from 25,000 gallons in 1981 to 400 gallons in 1982) was realized.[1]

Case No. 12: Daly-Herring, Kinston, N.C.--Daly-Herring is a pesticide manufacturer, producing dusts containing a variety of organic chemicals (mainly pesticides) which are all controlled by a single baghouse. The company installed separate baghouses to control their two production lines to permit economic recycling of some of the segregated materials. The savings accrued by this practice is estimated to be $2,000/year for materials conserved and $9,000/year for reduced disposal costs.[1]

5.1.6 Source Reduction Summary

Source reduction involves a wide variety of practices, some of which may be applicable at virtually any plant generating solvent wastes. Because the potential application of these practices is so diverse, there are little documented data which indicate the significance of waste source reduction on nationwide industrial waste generation patterns. The EPA and other State agencies believe that some form of source reduction is applicable to most industrial plants generating hazardous wastes and will result in a significant reduction in waste generation as more companies implement waste minimization programs.[5]

Review of documented case studies on source reduction indicates that these practices have been applied in more instances to solvent wastes than any other waste type. Additionally, it appears that source reduction practices are used more frequently for chlorinated solvents, especially 1,1,1-trichloroethane and methylene chloride. With respect to cost savings, the data appear to indicate that source reduction of large generating sources may yield annual savings of tens of thousands of dollars. Savings in the hundreds of thousands of dollars may even be possible if source reduction practices allow for the elimination of unit operations such as air pollution controls.

Regulatory trends appear to be moving towards the promotion of source reduction at sites generating hazardous wastes. The EPA has recently proposed requirements that generators certify institution of hazardous waste reduction programs (51 FR 10177, March 24, 1986). This would involve the institution at generator sites of programs to reduce the volume or toxicity of hazardous wastes to a degree determined by the generator to be economically practicable. Generators must also certify that their current method of management is the most practicable method available to minimize present and future threats to human health and the environment. Three States currently have established source reduction/pollution prevention programs: North Carolina, Minnesota, and Massachusetts. In addition, Tennessee has established a "pilot program", and Kentucky, California, Maryland, and Washington have programs currently in development. These programs vary from state to state but, in general, include information exchange, technical assistance, and economic incentives to companies to encourage development of their programs.[6]

5.2 RECYCLING/REUSE

According to EPA guidance issued on January 4, 1985, "recycling" was defined as practices in which wastes are: (1) reclaimed, or (2) reused. A reclaimed waste is one which is processed or treated through some means to purify it for subsequent reuse, or to recover specific constituents for reuse. Reused wastes are those which serve directly as feedstocks, without any treatment. Recycling of wastes may be done by either the original generator or other firms. This section discusses the various advantages and disadvantages of the available technologies for spent solvent waste recycling, and the potential consequences of their application to specific waste types.

Of the major classifications of hazardous wastes, solvents are recycled most often.[6] Based on information provided by the National Association of Solvent Recyclers, significant volumes of the following 11 solvents have been recycled:[7]

xylene
toluene
acetone
methyl ethyl ketone
1,1,1-trichloroethane
methylene chloride
methanol
perchloroethylene
trichloroethylene
methyl isobutyl ketone
isobutanol

Volumes of various solvent waste types recycled have been discussed in Section 3.3. Roughly 80 percent of solvent recycling occurs in onsite facilities.

5.2.1 Recycling Technologies

The most common solvent waste recycling technologies are distillation, settling, decanting and filtration, and solvent extraction, with distillation the most prevalent. A compilation of documented solvent recycling practices is shown in Table 5.2.

Solvent recovery technology commonly includes three types of operating systems: distillation; solvent extraction; and adsorption. The key to the effective performance of any solvent recovery system lies in the characteristics of the solvent itself. Solvents which are more volatile, for example, will be readily recovered through distillation. A wide variety of treatment systems exists for recovery of solvents, most of which are discussed in detail in other chapters of this report. A brief summation of several important solvent recovery technologies is provided below. Further detail is provided in Section 7.

Distillation--

Distillation is a liquid separation process which takes advantage of differences in the relative volatilities of constituents present in a process stream. The products obtained from this process can possess relatively high levels of purity. The most common distillation processes are:

- Batch Distillation--Batch distillation is the simplest available distillation system, consisting of an evaporator followed by a condenser. This process is generally effective and economical for solvents with low solid content (<5 percent) and low viscosity.[7] Between 50 and 95 percent of the solvent can be recovered by batch distillation.[6] The still bottom products from batch distillation of halogenated solvents can contain 20 to 40 percent halogenated solvents.[8]

  Batch distillation is widely used onsite by operations such as dry cleaners, print shops, and metal degreasing operations that do not have high solvent volume demands . Studies show that for streams containing 3,000 to 6,000 ppm chlorinated hydrocarbon, removal efficiencies of up to 90 percent have been obtained.[9] Distillation is not recommended for certain spent solvents (e.g., mixtures of toluene and methyl ethyl ketone from plastic and paint manufacturers) which contain resinous materials which polymerize on still walls or coil surfaces and reduce heat-exchange efficiency.[10]

TABLE 5.2. SUMMARY OF DOCUMENTED SOLVENT RECYCLING PRACTICES[a]

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Manufacture wood office furniture	2521	Still used to recycle acetone Added to reclaimed solvent and this reconstituted mix is used as a thinner	Onsite	Spent lacquer thinner	Bowling Co., Mt. Olive, N.C.
Polyester resin and fiber plants	2824	Distillation (tolling arrangement)	Offsite	Dowtherm (solvent)	Celanese Fiber Operations, Charlotte, N.C.
Cellulosics plant	2823	Bench scale distillation process to separate solvent from oil	Onsite	Freon TMC® (solvent)	Celanese Fiber Operations, Charlotte, N.C.
Industrial organic chemicals	286	Fractional distillation		Halogenated still bottoms	Not documented
Printing industry	27	Collection in a still, followed by distillation (still bottoms incinerated)	Onsite	Xylene contaminated with paint	Lenoir Mirror, Co., Lenoir, N.C.
Dry cleaning operations at a paint shop	9711	Nonfractionating batch still	Not given	Waste solvents (including: mineral spirits, ketones, and epoxy thinners containing paint pigments)	Norfolk, NSY, Norfolk, VA
Printing and publishing	2751	Collected in a still and reclaimed (reused for cleanup with virgin materials)	Not given	Alcohol/acetate mixture	Rexham Corp., Greensboro, N.C.
Manufacture coatings (including water and solvent based paints)	2851	Spent solvent continuously pumped into still. Solvent is distilled (primarily reused for equipment cleanup)	Onsite	Spent solvent (primarily toluene and xylene)	Southern Coatings, Sumter, S.C.

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Manufacture solvent based inks for retro-gravure printing	2893	Still used to collect solvent (reclaimed solvent used twice for cleaning equipment before redistillation)	Onsite	Spent isopropyl acetate	Thiele-Engdahl, Winston-Salem, N.C.
Maintaining aircraft, helicopters and missiles	9711	Batch atmospheric pressure stills (single-stage batch still; water separator & electrically powered steam generator)	Onsite	Trichloroethane, Freon-113, isopropanol (a new still has been installed to reclaim PD-680 dry cleaning solvent, silicon damping fluid, paint thinners, and collanol 25R fluid)	Warner Robins AFB, Macon, GA
Production of electric meters	3825	Closed-loop continuous distillation units (from vapor degreasing operations)	Onsite	Dow stabilized perchloroethylene and Freon TMS degreaser	Westinghouse Electric Meter Plant, Raleigh, NC
DOD base		Distillation (incineration if contaminated)	Onsite	Freon Type 2	DOD Base
Paint thinning	2851	Single stage distillation to separate volatile solvent from paint thinners	Not given	Paint thinners	DOD Base
Photographic equipment	3861	Fractional distillation	Not given	Solvents, halogenated	Not documented
Machinery	35	Fractional distillation	Not given	Solvents, halogenated	Not documented

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Pesticide & agricultural chemicals	2879	Fractional distillation	Not given	Solvents, halogenated	Not documented
Plastics & synthetics	282	Fractional distillation	Not given	Solvents, halogenated and nonhalogenated	Not documented
Stone, glass, clay	32	Fractional distillation	Not given	Solvents, nonhalogenated	Not documented
Industrial organic chemicals	286	Fractional distillation	Not given	Solvents, nonhalogenated	Not documented
Pharmaceuticals	283	Fractional distillation	Not given	Solvents, nonhalogenated	Not documented
Paint & allied products	285	Fractional distillation	Not given	Solvents containing heavy metals	Not documented
Industrial organic chemical & chemical preparation industry	286	Distillation (often tolling arrangement)	Offsite	Solvents	Not documented
Electronics & machinery industry	36	Distillation (often tolling arrangement)	Offsite	Solvents	Not documented
Petroleum refining industry	2911	Distillation (often tolling arrangement)	Offsite	Solvents, nonhalogenated	Not documented
Transportation equipment industry	40	Distillation (often tolling arrangement)	Offsite	Solvents, nonhalogenated	Not documented

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Chemical preparation industry	2899	Distillation (often tolling arrangement)	Offsite	Solvents, nonhalogenated	Not documented
Electronics industry	362	Distillation (often tolling arrangement)	Offsite	Solvents, nonhalogenated	Not documented
Machinery industry	35	Distillation (often tolling arrangement)	Offsite	Solvents, nonhalogenated	Not documented
Parts cleaner service (cleaning equipment with solvents)	2842	Settling followed by distillation for solvents - bottom oils blended for fuel	Offsite (for generators)	Solvents	Not documented
Manufacture wood office furniture	2521	Heat recovery	Onsite	Spent lacquer thinner used for heat recovery	Bowling Co., Mt. Olive, NC
Wood and Furniture industry	2521	Heat recovery	Onsite	Heat recovery using spent solvents (toluene, xylene, acetone, ethanol, butanol, isopropyl alcohol, neptha, methyl ethyl ketone & esters)	Burlington Furniture Co., Lexington, N.C.
Cellulose acetate fiber plants (spinning process)	2823	Concentrate MeO/acetone and send to off-site kiln for heat recovery	Offsite	Heat recovery using concentrated MeO/acetone mix	Celanese Fiber Operations, Charlotte, N.C.

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Chemical & allied products (cosmetics)	2844	20% hydro-alcoholics used in fuel (modified steam & hot water boilers)	Onsite	Heat recovery using hydroalcoholics	Coty Div., Pfizer Inc., Stanford, N.C.
Chemical distributor & recycler	5161	Residue from recycling is blended and used as a fuel	Offsite (for generators)	Residue is blended with other hydrocarbons and sold as fuel for cement kilns	Hukill Chemical Corp., Bedford, OH
High tech printing and coating	27	Heat recovery	Onsite	Methyl ethyl ketone vapors burned for heat recovery	Rexham Corp., Matthews, N.C.
Multidivisional manufacturing	3861	Fuel supplement in existing boiler	Onsite	Solvent laden air (predominantly heptane)	3M, Minneapolis, MN (headquarters)
Wood & furniture industry	25	Heat recovery	Onsite	Spent solvents	Not documented
Paint, coatings & ink industry	2851 2893	Heat recovery	Onsite	Spent solvents	Not documented
Industrial organic chemical & chemical preparation industry	286	Use in cement kilns for heat recovery	Offsite	Solvents	Not documented
Electronics and machining industry	36	Use in cement kilns for heat recovery	Offsite	Solvents	Not documented
Petroleum refining	2911	Heat recovery	Offsite & onsite	Solvents, non-halogenated	Not documented

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Transportation equipment	40	Heat recovery	Offsite & Onsite	Solvents, non-halogenated	Not documented
Electronics	36	Heat recovery	Offsite & Onsite	Solvents, non-halogenated	Not documented
High tech printing & coating	27	Solvent vapors recovered & sold to coating industry	Onsite	Solvent vapors (toluene)	Rexham Corp., Matthews, N.C.
Recondition used tanks and other armored vehicles (removal of paint, grease, oil, rust, and oxides)	9711	Vapor degreasing units equipped with distillation solvent recovery system	Onsite	Trichloroethylene	Anniston Army Depot
Printing process, paper & allied products	2653	Recovery of vaporized solvent	Onsite	Vaporized solvent	RJR Archer, Inc., Winston-Salem, N.C.
Multidivisional manufacturing	3861	Condensation of vapors from drying oven exhaust	Onsite	Hydrocarbons	3M, Minneapolis, MN (headquarters)
Tape manufacturer	2295	carbon adsorption systems - after adsorption & desorption processes the solvent is decanted from water and reused	Onsite	Toluene	Shuford Mills, Hickory, N.C.
Multidivisional manufacturing	3861	Carbon adsorption	Onsite	Solvents	3M, Minneapolis, MN (headquarters)

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Industrial organic chemical	286	Carbon adsorption	Onsite & Offsite	Solvents, non-halogenated	Not documented
Chemical preparation industry	2899	Carbon adsorption	Onsite & Offsite	Solvents, non-halogenated	Not documented
Oil refining industry	2911	Carbon adsorption	Onsite & Offsite	Solvents, non-halogenated	Not documented
Electronics industry	362	Carbon adsorption	Onsite & Offsite	Solvents, non-halogenated	Not documented
Plastics industry	30	Carbon adsorption	Onsite & Offsite	Solvents, non-halogenated	Not documented
Multidivisional manufacturing (film developing)	3861	Gravity separation	Onsite	Solvents	3M, Minneapolis, MN (headquarters)
Industrial organic chemicals	286	Steam stripping	Onsite & Offsite	Solvents, nonhalogenerated & halogenated	Not documented
Plastics industry	30	Steam stripping	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Chemical preparation industry	2899	Steam stripping	Onsite & Offsite	Solvents, nonhalogenated	Not documented
Oil refining industry	2911	Steam stripping	Onsite & Offsite	Solvents, nonhalogenated	Not documented

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Electronics industry	362	Steam stripping	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Aerospace industry	9661	Steam stripping	Onsite & Offsite	Solvents, halogenated	Not documented
Hazardous waste management facility		Solvent extraction followed by a flash evaporator and calcium chloride adsorption bed	Onsite	Waste solvent containing typically 85% methylene chloride and 15% isopropyl alcohol to obtain saleable quality methylene chloride (98-99% pure)	Silresin Chemical Corp., Lowell, Mass.
		Distillation to remove oil; followed by solvent extraction to reclaim solvent	Onsite	Waste material of oil, freon and other solvents; freon is extracted after oil has been removed	Not documented
Industrial organic chemicals	286	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Plastics industry	30	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Chemical preparation industry	2899	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Oil refining industry	2911	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Electronics industry	362	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Aerospace industry	9661	Solvent extraction	Onsite & Offsite	Solvents, nonhalogenated and halogenated	Not documented
Naval Air Rework Facility	9711	Settling and straining to remove dirt oil & water-based cooling emulsion separated by a centrifuge	Onsite	Water-based cooling emulsion (e.g., Trimsol, Simcool)	Pensacola Naval Air Rework Facility, Pensacola, FL
Manufacture trade sales paints	5198	Waste reuse-wash solvent from each batch is collected in drums, waste solvent from previous cleanup is used in the manufacturing process	Onsite	Waste solvent	Desoto, Greensboro, N.C.
High tech printing & coating	27	Cleanup toluene is segregated by ink type and reused as a thinner	Onsite	Spent toluene (from press and roller cleanup)	Rexham Corp., Matthews, N.C.
Produces coatings for fiberglass	3296 or 2221	Solvent recycling	Offsite	Spent acetone (from cleanup process)	American Colors, Charlotte, N.C.
Magnetic tape facility	3679	Nitrogen-based solvent recycling system (with this system higher concentration levels can be obtained safely for solvent recovery)	Onsite	Tetrahydrofuran	Airco Industrial Gases, Murray Hill, N.J. (facility located in CA)

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Cellulose acetate fiber plants (spinning process)	2823	Recovery and recycle of acetone	Onsite	Acetone	Celanese Fiber Operations, Charlotte, N.C.
Flushing refrigerant through shipboard refrigeration units	9711	"Flushing rig" made of spare parts used to clean impurities out of refrigerant and the refrigerant is recirculated through the system	Onsite	Refrigerant	Charleston NSY, Charleston, N.C.
Solvent Recycler	7399	Use still bottoms to make a low-grade paint (residue is reused either as a fuel supplement or as a source of pigments & resins for the paint industry)	Offsite (for generators)	Still bottoms from paint Romulus, MI	Chemical Recovery Systems,
Chemical distributor and recycler	5161	Batch tolling or purchase waste solvents outright	Offsite (for generators)	Accepts wide range of solvents	Hukill Chemical Corp., Bedford, OH
Manufacture coatings for furniture industry	2851	Solvent recycling	Offsite	Low boiling point solvents (including ketones, esters, aliphatics & aromatics)	Lilly, High Point, N.C.
		Solvent recycling	Onsite	Hydrocarbon thinners & solvents, fluorocarbons, freons & esters	Oil & Solvent Processing Co., Azusa, CA

TABLE 5.2 (Continued)

Production process/ industry type	SIC code	Type of solvent recovery	Location	Waste recycled/ recovered	Industrial precedent
Printing	27	Flexoprinter reclaims useable solvents from waste inks	Onsite	Solvents	Rexham Corp., Greensboro, N.C.
		Solvent recycling	Onsite	Solvents	Romic Chemical Co., Palo Alto, CA
		Solvent recycling	Onsite	Solvents	Solvent Services, San Jose, CA
Pesticide manufacturing (using organic solvent media)	2879	Solvent recovery for reuse for equipment cleaning	Onsite	Solvents	Not documented
Industrial organic chemicals	286	Distillation, evaporation, filtration	Onsite	Solvents from degreasing and dry cleaning	Not documented
Chemical preparation industry	2899	Distillation, evaporation, filtration	Onsite	Solvents from degreasing and dry cleaning	Not documented
Electronics & machinery industry	36	Distillation, evaporation filtration	Onsite	Solvents from degreasing and dry cleaning	Not documented
Petroleum refining industry	2911	Distillation, evaporation filtration	Onsite	Solvents, nonhalogenated	Not documented
Transportation equipment industry	40	Distillation, evaporation filtration	Onsite	Solvents, nonhalogenated	Not documented

[a]Source: Versar, 1985. Reference 6.

- Separators--There are two types of separators used to recover spent solvents. Scraped-surface separators are well suited for solvent streams with a high concentration of suspended solids and sludges and can be effective in separating spent solvent fractions by density.[10] The other type of separator is the thin (falling) film separator. Thin film separators are best suited for reclaiming low boiling point (150 to 200°C) solvents and are not applicable to spent solvents containing suspended or dissolved resinous materials. Both types of separators can be used independently or as a pretreatment step prior to distillation columns.[6,10]

- Distillation (Fractionation) Columns--Distillation columns are employed when a high purity product (typically solvent contents greater than 90 percent) is required. The feedstock stream has to be a free-flowing fluid with negligible solids content. Pretreatment is usually required prior to this process.

  Two types of distillation columns exist, plate columns and packed columns. By installing intermediate drawoff levels on plate columns, a number of mixed solvents can be recycled at one time if they have boiling ranges separated by approximately 20 to 30°C.[10] Packed columns usually result in a higher quality solvent but are more susceptible to fouling. The choice between these two types of distillation columns is usually based on economics.[6]

Solvent Extraction--

In solvent extraction, a solute is transferred from one liquid phase to a second immiscible phase. The operation can be conducted as a batch process or by contact of the solvent with the feed in staged or continuous contact equipment. Solvent extraction is most suitable for recovering organic solvents from aqueous waste streams.[9] The costs for solvent extraction will be highly dependent on the value of the recovered organics for concentrated solvent wastes.

Adsorption--

Adsorption is a well established separation process. For the purpose of recovering spent solvent, activated carbon and resin systems should be considered. The major distinction between the two systems is the type of adsorbent regeneration process employed. Resin regeneration is generally easier and can be achieved using rinse waters and solvents, whereas high temperature furnaces are usually required to drive off the sorbate from the carbon surface. Both carbon and resin systems require the feedstock stream to be a single liquid phase. The solid content in feedstocks should be less than 50 ppm and may, in some cases, have to be below 10 ppm to prevent bed clogging.[9]

Many solvents, especially low boiling point chlorinated solvents are readily reclaimed using an activated carbon adsorption system. However, the major application of adsorption systems to date has been confined to dilute aqueous streams.[9]

Purification--

When high purity of recovered products is required, further purification processes become necessary to increase the solvent content of the final product. Purification processes may include fractionation columns, further decanting with additional cooling to increase separation or drying through a desiccant or salt bed. Some solvents must be treated with additives to restore their buffering capacity.[13]

5.2.2 Selection of Recycling Technology

The economic benefits of recycling a wastestream or mixture of waste streams are dependent upon the physical and chemical characteristics of the waste stream and the quantity of waste to be recycled.

The physical and chemical characteristics of the waste determine the technical constraints of the process including raw materials, handling and pretreatment, and operating parameters of the system such as temperatures and pressures. In general, physical form determines whether or not a process can be used whereas chemical characteristics affect ease of separation and selection of optimal processing conditions.

The types of constituents in a waste will influence its reactivity, volatility, and adsorbability. The most significant constituents to consider are halogens (especially chlorine), metals, other solids and moisture which present particular limitations on certain technologies. Most recycling technologies have practical limits on their capability of handling high solids, viscous and polymerizable materials. Pretreatment through the use of physical separation processes (e.g., filtering, decanting, settling, skimming, centrifuge) is common in recycling applications. Similarly, post treatment processes may be required to bring recycled materials up to process specifications. Typical post treatment methods include decanting, dehydrating and fractionation.

The quantity of waste to be recycled is also a significant factor in the selection of an appropriate recycling technology. Waste quantity will determine the size of equipment, volume of raw materials to be used in recycling (e.g., carbon for carbon adsorption), and pollution control and disposal requirements. Certain technologies may be preferable for small quantity processing but, in general, the larger the quantity of waste to be recycled, the more economically attractive recycling becomes.

Economic considerations play a major role in determining the recyclability of a solvent hazardous waste. The primary economic considerations are the capital and operating costs of the recycle system, disposal costs and value of recovered solvent. Among the recovery technologies discussed earlier, solvent extraction processes have the highest capital and operating costs, due to their high demand for extraction agents and associated equipment, while adsorption systems are probably the least expensive. Disposal costs and value of recovered solvent become increasingly important as waste volume increases. If recovered products are used onsite, their value is reflected in the reduced demand for virgin raw materials. If sold for offsite use, their value is dependent on the market price of virgin solvent and the degree of purity. Typical prices of recovered solvent range from 50 to 90 percent of the price of virgin materials (see Table 4.1.2).

Another option to be considered in selecting a recycling technology is whether the operation should be conducted onsite, or at an offsite facility such as a commercial recycler. The choice between onsite and offsite recovery is dependent on many factors including recycling costs, volume of spent solvent generated, availability of equipment, personnel and markets, facility size, technical capability of personnel, and use of recovered solvent.

Transportation cost must also be considered for offsite recycling. The cost for transportation is a function of the distance from the generating facility to the recycling facility, the volume of the waste being transported, and the transportation method used. Generators of low volumes of wastes can significantly reduce their handling and transportation cost by participating in cooperative storage arrangements with other small quantity generators of similar wastes. A good example is the Neighborhood Cleaners Association (NCA) collective recycling program.[6] Under NCA's new recycling program, a contractor has been hired to collect and recycle perchloroethylene solvent wastes which were previously landfilled by 1,400 dry cleaning facilities. Part of this program's success results from the chemical compatibility of the waste streams collected from the dry cleaners.

In addition to purely economic factors, the size of a facility and its technical expertise may also influence the decision to recycle solvents onsite or offsite. Large facilities usually have the advantage of a strong technical staff to manage onsite recovery. However, onsite recovery has been found to be a competitive option to offsite recovery for both small and large generators.

Ultimate selection of a recycling technology will be highly site specific. A selection methodology has been presented in Section 14.0 outlining economic and other considerations. Details on costs and capabilities of specific recycling technologies can be found in Section 7.0.

5.2.3 Reuse

Certain solvent hazardous wastes generated by an industrial process may be directly used for a different purpose in another process. Examples of direct reuse of spent solvents include wastes used in precleaning and wastes fired as fuel in high temperature industrial processes. Reused wastes have the advantage of much lower costs relative to use of virgin materials. In general, reusable wastes are produced by large manufacturing operations, or those which require high purity, and are consumed by smaller, often batch processors, which do not necessarily require high levels of purity in feedstocks. Reused wastes are usually only slightly contaminated, but several instances have been documented which where involve reuse of wastes with only 60 to 70 percent solvent content.[10]

Three primary factors should be considered when evaluating reuse as a potential waste management option. First, the ability to reuse a solvent waste depends upon its chemical composition and effect of the various waste contaminants on the reuse practice. Second, the economic value of the reused waste must justify the expense incurred in changing a process to accommodate it. Third, the availability of the waste must be considered. A processor using a secondary material must be sure that the material will be available to satisfy his demand.

Reuse of wastes may be accomplished either by the generator itself, or through sales to a different processor. Marketing of wastes for reuse is often facilitated through use of waste exchanges. Waste exchanges are institutions which serve as brokers of wastes or clearing houses for information on wastes available for reuse. In some waste exchanges, potential buyers of wastes are brought into contact with generators, while other waste exchanges accept or purchase wastes from a generator for sales to other users. Waste exchanges are considered by EPA to be of great potential value in future waste management because through waste exchanges, recycling practices may be increased.[12]

A wide variety of wastes have been recycled via the waste exchange system. A listing of solvent hazardous wastes available through two waste exchanges is presented in Table 5.3. Solvent wastes are among those which have been sought most highly, due to their versatile reuse potential.[6]

In general, the "exchangeability" of a waste is enhanced by higher concentration and purity, quantity, availability, and higher offsetting disposal costs. Some of the limitations to waste exchangeability are the high costs and other difficulties associated with transportation and handling, costs of purification or pretreatment required and in certain cases, the effect on process or product confidentiality. In general, waste exchange involves transfer of products from large, continuous processors to small, batch processors, manufacturing products from basic chemical manufacture to chemical formulators, or products from high purity processors (e.g., pharmaceutical manufacturers) to low purity processors (e.g., paint manufacturers).

TABLE 5.3. SUMMARY OF SOLVENTS RECYCLED VIA TWO WASTE EXCHANGES

Type of wastes	Waste exchange[a]	Time period	Quantity (tons)(3)	Distance hauled (miles)	Estimated $ value
Solvents	IME	1985	639.3	--	937,960
Organics/solvents	NEIWE	1983			
Carbon tetrachloride	NEIWE	1983	0.9	400	396[b]
Ethanol	NEIWE	1983	3.8	450	400
Lacquer solvent	NEIWE	1983	Unknown	200	875
Mixed solvents	NEIWE	1983	75.0	200	16,000
Paint & ink wash solvents	NEIWE	1983	8.3	50	2,000
Paint solvents	NEIWE	1983	27.5	175	20,000
Phenol	NEIWE	1983	0.3	5	250
Polydimethylsiloxane	NEIWE	1983	2.7	175	3,000
Trichloroethane	NEIWE	1983	3.4	375	1,500
Trichloroethylene	NEIWE	1983	4.2	60	2,000
Acetone[c]	NEIWE	6/81-12/81	0.6	75	208
Solvents[c]	NEIWE	6/81-12/81	10	125	2,040
Trichloroethylene[c]	NEIWE	6/81-12/81	3	75	None
Trichloroethane[c]	NEIWE	6/81-12/81	3	25	1,100
Solvents	NEIWE	6/81-12/81	55	250	10,000
Ethylene glycol	NEIWE	6/81-12/81	5	75	3,000
Solvents	NEIWE	6/81-12/81	142	150	39,000
Mixed ethylene glycols	NEIWE	6/81-12/81	16	Unknown	Unknown
Trichloroethane	NEIWE	6/81-12/81	3	Unknown	2,992
Paint thinner	NEIWE	2/82-2/83	42	175	14,000
Trichloroethane	NEIWE	2/82-2/83	2	75	385
Alcohols	NEIWE	2/82-2/83	Unknown	Unknown	Unknown
Solvents	NEIWE	2/82-2/83	210	Unknown	110,000

[a] IME = Industrial Material Exchange.

NEIWE = Northeast Industrial Waste Exchange.

[b] Unit cost estimate obtained from Chemical Marketing Reporter, May 28, 1984 issue.

[c] One-time only transaction.

Source: Versar 1985. Reference 6.

Waste exchanges are operated by both private firms and public organizations. Several waste exchanges are listed below:

- California Waste Exchange (California);
- Canadian Waste Materials Exchange (Ontario);
- Chemical Recycle Information Program (Texas);
- Colorado Waste Exchange (Colorado);
- Georgia Waste Exchange (Georgia);
- Great Lakes Regional Waste Exchange (Michigan);
- Industrial Materials Exchange Service (Illinois);
- Industrial Waste Information Exchange (New Jersey);
- Inter-Mountain Waste Exchange (Utah);
- Louisville Area Waste Exchange (Kentucky);
- Midwest Industrial Waste Exchange (Missouri);
- Montana Industrial Waste Exchange (Montana);
- Northeast Industrial Waste Exchange (New York);
- Piedmont Waste Exchange (North Carolina);
- Southern Waste Information Exchange (Florida);
- Techrad (Oklahoma);
- Tennessee Waste Exchange (Tennessee);
- Virginia Waste Exchange (Virginia);
- Western Waste Exchange (Arizona); and
- World Association for Safe Transfer and Exchange (Connecticut).

The following is a list of the private material exchanges currently in business:

- Zero Waste Systems, Inc. (California);
- ICM Chemical Corporation (Florida);
- Environmental Clearinghouse Organization - ECHO (Illinois);
- Americal Chemical Exchange - ACE (Illinois);
- Peck Environmental Laboratory, Inc. (Maine);
- New England Materials Exchange (New Hampshire);
- Alkem, Inc. (New Jersey);
- Enkarn Research Corporation (New York);
- Ohio Resource Exchange - ORE (Ohio); and
- Union Carbide Corporation (in-house operation only; West Virginia).

5.3 ADDITIONAL EXAMPLES OF WASTE MINIMIZATION PRACTICES

There is a growing incentive for companies to undertake waste minimization programs as a consequence of increasing waste disposal costs and liability. Besides protecting human health and the environment by drastically lowering the amount of waste generated, waste minimization programs can, in many cases, provide substantial economic benefits. Table 5.4 provides information concerning onsite waste reduction techniques employed at three major hazardous waste generators. The accomplishments, as measured by the percent reduction of wastes (mainly solvents), are impressive. Waste reductions and resulting dollar savings at a fourth company are shown in Table 5.5.

Finally, seven example case summaries describing waste recycling/reuse are provided below. Data describing net financial benefits is reported in most of these examples.

Case 1: 3M Electronics Products Division, Columbia, MO--3M is involved in film developing, in which a wastewater contaminated with 1,1,1-trichloroethane is produced. 3M installed a gravity decanter system to separate and subsequently recycle TCE. The process resulted in an annual savings of $12,000 (based on first year results), and also reduced their contamination of process water.[1]

Case 2: Celanese Fibers, Charlotte, NC--Celanese Fibers manufactures cellulosic fiber products. Solvents are used in a variety of operations, ranging from extractions to coatings. Solvent wastes are recycled both in-house and offsite. Laboratory solvents are recycled in-house in a bench-scale batch distillation process which separates Freon from finishing oil. An annual savings of $1,854 was reported. In another application, contaminated Dowtherm, which is used as a heat transfer medium, is sent to a distiller for regeneration. An annual savings of $163,765 was reported, which includes savings for materials and disposal.[4]

Case 3: Westinghouse Electrical Corporation Meter Plant, Raleigh, NC--Westinghouse Meter produces electrical meters for power plants. Three large vapor degreasers produce contaminated perchloroethylene solvents. These degreasers are equipped with continuous distillation to recycle clean solvents. The company estimates that the payback period for such units is 5 years.[4]

TABLE 5.4 EXAMPLES OF WASTE REDUCTION TECHNIQUES/ACCOMPLISHMENTS (ALL PROGRAMS ARE ONSITE)

Waste reduction method	Waste reduced		Percent reduced	Year program started	Description
	EPA number	Type			
Hewlett Packard					
Solvent conservation practices	F002 F003 F006	Halogenated solvents Alcohols Ketones	20	1983	Installed covers on sinks, increased freeboard.
Waste solvent recovery and oil recycling	F001	Halogenated solvents Cutting fluids	50	1982	Used distillation and centrifuge to reclaim materials for onsite use.
Conversion to water based paints	D001	Waste paints	30	1985	Water based paints have lower solvent content, are less hazardous, and create less air pollution.
Conversion from water wall paint booths to dry filters	D001	Paint sludge	100	1985	Wet paint booths create a liquid hazardous waste; dry filters are a solid waste and less volume.
Install sensors on photoresist bottle	F003	Solvents	20	1985	Sensor allows complete use of photoresist in bottle.
Eliminate phenolic stripper	F003	Phenolic stripper	100	1983	Conversion to dry etch process.
3M					
Waste recovery	D001	Solid		1983	Waste solvent recovered from distillation tower, still bottoms and skimming from wastewater holding tanks is used as boiler fuel.
Process modification	D001	Solid	77	1984	Core configuration was modified to remove resin deposit and a still was purchased to recycle methylene chloride used in cleanup.
Process modification	D001	Liquid	100	1984	Solvent was eliminated from the process.
Process modification	D001	Liquid	100	1984	Cleanup procedure for new latex adhesive compounding equipment developed.
Waste recovery	D001	Solid	50	1983	Recycle heptane instead of scrapping it.

TABLE 5.4 (continued)

Waste reduction method	Waste reduced		Percent reduced	Year program started	Description
	EPA number	Type			
3M (continued)					
Process modification	D001	Solid	50	1983	Process modifications preclude the need for one of two kettle cleanings, and subsequent discharge.
Product formation	D001	Solid	100	1982	A new starter solution containing no propanol was substituted for 3M's which contains propanol.
Waste recovery	D001	Solid	100	1983	Solvent is recovered from wet scrap via steam stripping and reused rendering scrap nonhazardous.
Recovery/reuse	D001	Solid	80	1985	Sludge recrystallized to recover reusable product.
Product modification	D001	Solid	60	1985	Reduction of defects in product resulted in less rejection.
Process modification	D001	Solid	80	1985	Teflon coated rolls eliminated scratches making cleanup easier and less product scrapped.
Process modification	D001	Solid	100	1985	Superior inline blender provided more stabilized adhesive viscosity reducing scrapped adhesive.
Recovery/reuse	D001	Solid	20	1985	Education program resulted in fewer destroyed drums containing nonpumpable waste.
Production reformulation	D001	Solid/Air	100	1985	Reformulated from a solvent based adhesive to a nonsolvent based adhesive.
Recovery/reuse	D001	Solid	100	1985	Excess solvent reclaimed.
Product reformulation	D001	Solid	100	1985	Reformulated to nonhazardous.
Product reformulation	D001	Solid	100	1985	Substitution of water base adhesive for solvent base.
Process modification	D001	Solid	50	1985	Confidential.

(continued)

TABLE 5.4 (continued)

Waste reduction method	Waste reduced		Percent reduced	Year program started	Description
	EPA number	Type			
3M (continued)					
Product reformulation	D001	Solid	100	1985	Change in process equipment resulted in rapid parts changing and cleaning.
Product reformulation	D001	Solid	60	1985	Solvent replaced with higher flash point solvents.
Product reformulation	D001	Solid	100	1985	Solventless adhesive replaced solvent based adhesive.
Product reuse	D001	Solid	100	1985	Waste previously incinerated now sold to customer for reuse.
Process modification	D001	Solid/Air	10	1985	Waste reduction by improved sampling techniques.
Process modification and redesign	D001	Solid	100	1985	Process and equipment improvement. Improved charging accuracy.
Product reformulation	D001	Solid/Air	50	1985	3M product replaced vendor product allowing reduction in solvent usage.
Process modification	D001	Solid	100	1985	Process changed from water addition to heating resulting in less product loss.
Process modification	D001	Solid	100	1985	Resin solutions that have a final viscosity under or over spec. are now used in making other products.

TABLE 5.4 (continued)

Waste reduction method	Waste reduced		Percent reduced	Year program started	Description
	EPA number	Type			
Eastman Chemical					
Abatement	D001	Liquid	100	1985	Substituted inflammable for flammable solvent.
Recycling	D001	Spent catalyst	100	1986	Catalyst reclaimed for reuse.
Recycling	D001 F003 F005	Liquid	99	1981	Recovery of solvent by distillation.
Recycling	F003 F005	Liquid	99	1983	Recovery of solvents by distillation.
Recovery	D001 F003 F005	Liquid	99	1981	Recovery of solvents by distillation.
Minimization	F001 F002 F005 K009 K010 D001	Liquid and Solid	99	1981	Incineration in rotary kiln.
Minimization	F001 F002 F003 F005 D001	Liquid and Solid	99	1981	Incineration in rotary kiln and liquid incineration.

Source: References 14 and 15.

TABLE 5.5. COST VS SAVINGS FOR WASTE REDUCTION PROGRAMS CARRIED OUT BY IBM CORPORATION AT VARIOUS LOCATIONS

WASTE REDUCTION

Location	year	10^3lbs	Cost of program	Savings
Austin, TX	1982	7,873	$24,441	$1,360,007
	1983	15,652	49,550	3,022,170
	1984	23,663	96,000	7,853,154
Boulder, CO	1982	11,748	492,327	3,094,077
	1983	11,870	1,028,350	4,028,511
	1984	--	--	--
East Fishkill, NY	1982	47,974	0	14,495,197
	1983	43,737	0	13,714,699
	1984	67,738	0	39,157,600
Oswego, NY	1982	786	13,710	7,910,000
	1983	728	0	11,320,000
	1984	644	0	11,320,000
Poughkeepsie, NY	1983	1,030	9,065	3,251,978
	1984	990	4,500	2,114,152

ONSITE WASTE RECYCLING (10^3lbs)

Location	1984	1985
Austin, TX	9,177	19,668
Boulder, CO	2,153	274
East Fishkill, NY	33,521	41,068
Oswego, NY	311	108
Poughkeepsie	495	675

Source: References 14 and 15.

Case 4: Southern Coatings, Sumter, SC--Southern coatings manufactures a wide variety of coatings including solvent-based paints. Equipment cleaning operations were producing a large volume of solvent wastes. The company installed a distillation unit to recover 100 gallons/hour solvent containing primarily toluene and xylene (also containing mineral spirits and VMP). The company achieved a payback period of nine months. They estimate a raw materials cost savings of $0.67/gallon solvent.[4]

Case 5: Rexham Corporation, Greensboro, NC--Rexham Corporation does printing and coating for a variety of applicators. Spent alcohol/acetate solvents are produced during these operations. The company purchased a batch distillation unit. They achieved a waste reduction of 60 percent in reclaiming the solvent mixture for use in reprocessing and in cleanup operations.[4]

Case 6: American Enka, (location unknown) American Enka is a nylon yarn production and research facility. They have found it is economically profitable and environmentally sound to recycle their waste isopropyl alcohol solvent in-house rather than having it recycled by an outside firm. They purchased a used distillation unit and, with appropriate modifications, American Enka is now saving $90,000/year. They have also been able to reuse the still bottom residues as an asphalt emulsifier in another produce line.[1]

Case 7: DeSoto Chemical, Greensboro, NC--Wash solvents from manufacturing operations are collected and stored. The solvents are then reused during the next batch operation.[6]

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SECTION 6.0

PRETREATMENT

Pretreatment, in general, includes any process which precedes a final treatment/recovery process. The purpose of the pretreatment step is to remove constituents which would interfere with a subsequent process step or to transform the waste in some other way that will make subsequent processing simpler. Certain technologies, such as gravity settling, filtration and flotation, are commonly labeled as "pretreatment" technologies. However, in actuality, almost any technology, including those discussed in subsequent sections, could serve as a pretreatment measure. For example, pretreatment of a waste solvent may involve batch evaporation to remove dissolved solids. Following this pretreatment measure, the recovered solvent (volatile fraction) may then be fractionated to separate one or several reusable components. Another example of the use of a "final" treatment technology as a "pretreatment" measure involves the biological treatment of an aqueous leachate stream prior to carbon adsorption as shown in Figure 6.1. In this particular case, the purpose of carbon adsorption is to remove toxic chlorinated organic compounds, however in addition to these compounds the waste stream contains a large fraction of easily biodegraded organic compounds. Biological degradation of these compounds prior to adsorption reduced the organic load to the adsorbers, thus lowering the carbon usage rate and cost, and produces an effluent of equal quality.[1]

Therefore, pretreatment of a waste stream will be highly waste stream specific: various combinations of processes may be used depending on the characteristics of the waste and the requirements of the final treatment process. In general, pretreatment measures may be broken down into several

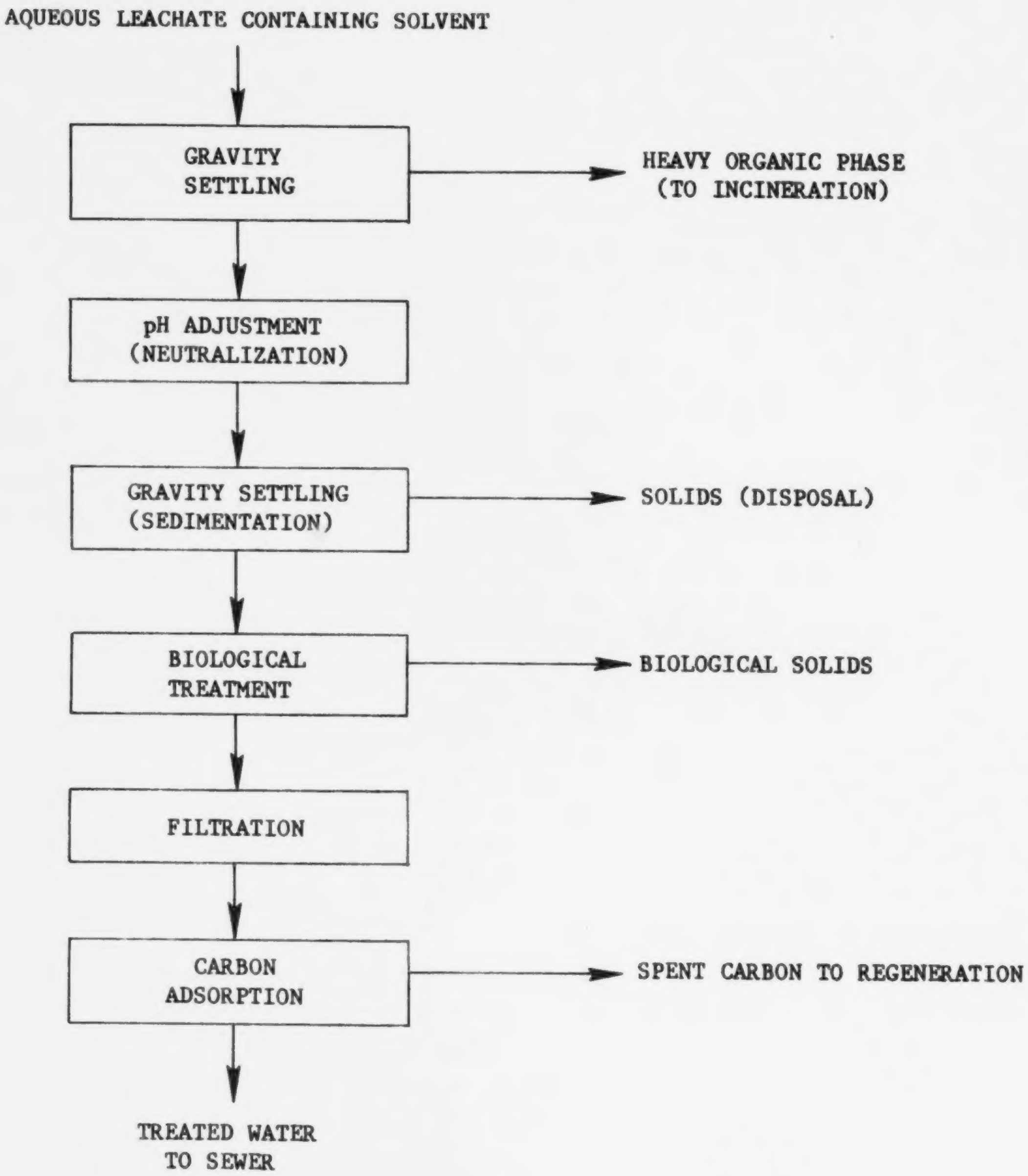
AQUEOUS LEACHATE CONTAINING SOLVENT
GRAVITY SETTLING
HEAVY ORGANIC PHASE (TO INCINERATION)
pH ADJUSTMENT (NEUTRALIZATION)
GRAVITY SETTLING (SEDIMENTATION)
SOLIDS (DISPOSAL)
BIOLOGICAL TREATMENT
BIOLOGICAL SOLIDS
FILTRATION
CARBON ADSORPTION
SPENT CARBON TO REGENERATION
TREATED WATER TO SEWER

Figure 6.1. Process train for treating aqueous/organic leachate.

categories based on the type of waste stream or constituent for which they are most applicable. Depending upon the categorization scheme used, these categories could consist of wastes with the following characteristics:

1. Liquid wastes containing suspended or floating materials
2. Solid/sludge wastes containing liquids
3. Inorganic solid wastes containing low levels of organics
4. Bulky, non-uniform solid wastes
5. Low heat content or high viscosity liquids

Certain technologies or techniques, including sedimentation, flotation, filtration, mixing, blending, crushing, and screening, are used to pretreat wastes with these characteristics prior to final treatment. The theoretical principles of these technologies are discussed in many texts on unit operations.[2,3,4,5] Therefore, one should consult these references if further detail is desired. The application of the technologies to the five waste types are discussed below.

6.1 LIQUIDS CONTAINING SUSPENDED OR FLOATING MATERIALS

This may be one of the most common situations where pretreatment is required. Many treatment processes require that suspended solids, oils and greases be removed prior to feeding into the unit. For example, granular carbon adsorption generally requires that the influent contain less than 50 ppm suspended solids and less than 10 ppm of oil and grease.[6,7] Common methods of removing these materials include screening, sedimentation, and flotation. Screening, sedimentation and filtration will remove suspended materials that are more dense than the liquid phase, while flotation will remove those that are less dense such as oil. In addition, dissolved air flotation (DAF) may be used to remove solids with specific gravities close to that of water, and emulsified materials. Settling, or decantation, is also a commonly used pretreatment to separate water from contaminated solvents prior to evaporation or distillation as shown in Figure 6.2. In this case, gravity

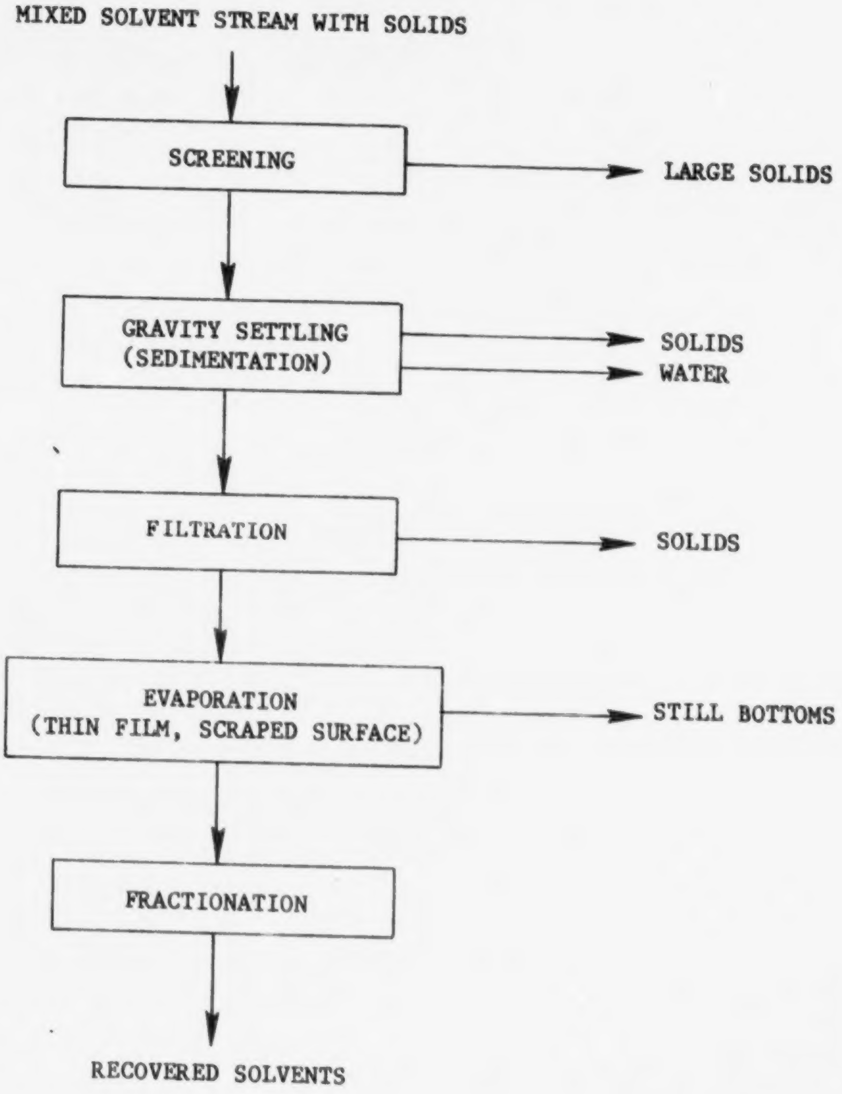
MIXED SOLVENT STREAM WITH SOLIDS
SCREENING
LARGE SOLIDS
GRAVITY SETTLING (SEDIMENTATION)
SOLIDS
WATER
FILTRATION
SOLIDS
EVAPORATION (THIN FILM, SCRAPED SURFACE)
STILL BOTTOMS
FRACTIONATION
RECOVERED SOLVENTS

Figure 6.2. Process train for treating waste solvent.

settling will result in a bottom layer consisting of organic solvent and an aqueous layer above. The organic solvent layer is then distilled and the aqueous layer is sent to the wastewater treatment plant to remove residual organics using biological treatment or carbon adsorption.

6.2 SOLID/SLUDGE WASTES CONTAINING LIQUIDS

Frequently sludges or other solids are contaminated with free liquids, primarily water. To reduce the volume of waste that must be treated, the waste can be dewatered. Methods for accomplishing this include vacuum filtration, centrifugation, and use of a filter press. The most common application of these processes is to wastewater treatment sludges. Solids are settled out of a wastewater stream in a sedimentation tank; the sludge formed at the bottom will generally have a solids content of about five percent. This sludge can then be dewatered using a vacuum filter centrifuge or a filter press. These dewatering units will generally produce a sludge with ten to 40 percent solids depending on the specific process used and the type of sludge. The liquid stream from the dewatering process will probably be recycled through the wastewater treatment process while the thickened sludge can then be incinerated or otherwise disposed. The dewatering of a sludge from five percent solids to 30 percent solids will not only reduce the volume significantly (from 40,000 lbs. to 6,600 lbs. for 1 ton of solids), but if the sludge is incinerated much less auxiliary fuel will be required to evaporate the entrained water.

6.3 INORGANIC SOLID WASTES CONTAINING LOW LEVELS OF ORGANICS

Solids are sometimes contaminated by low levels of organic compounds. In most cases, wastes of this form are hazardous only due to the organic contamination. Nevertheless, a common method of treatment is to incinerate the entire waste matrix. This is extremely expensive because a large amount of energy is required to heat up the non-combustible matter. It is much more desirable to extract the contaminant from the solid portion of the waste, and to incinerate only this portion as shown in the right-hand side of Figure 6.3. Extraction of contaminants from solids such as soil is similar in

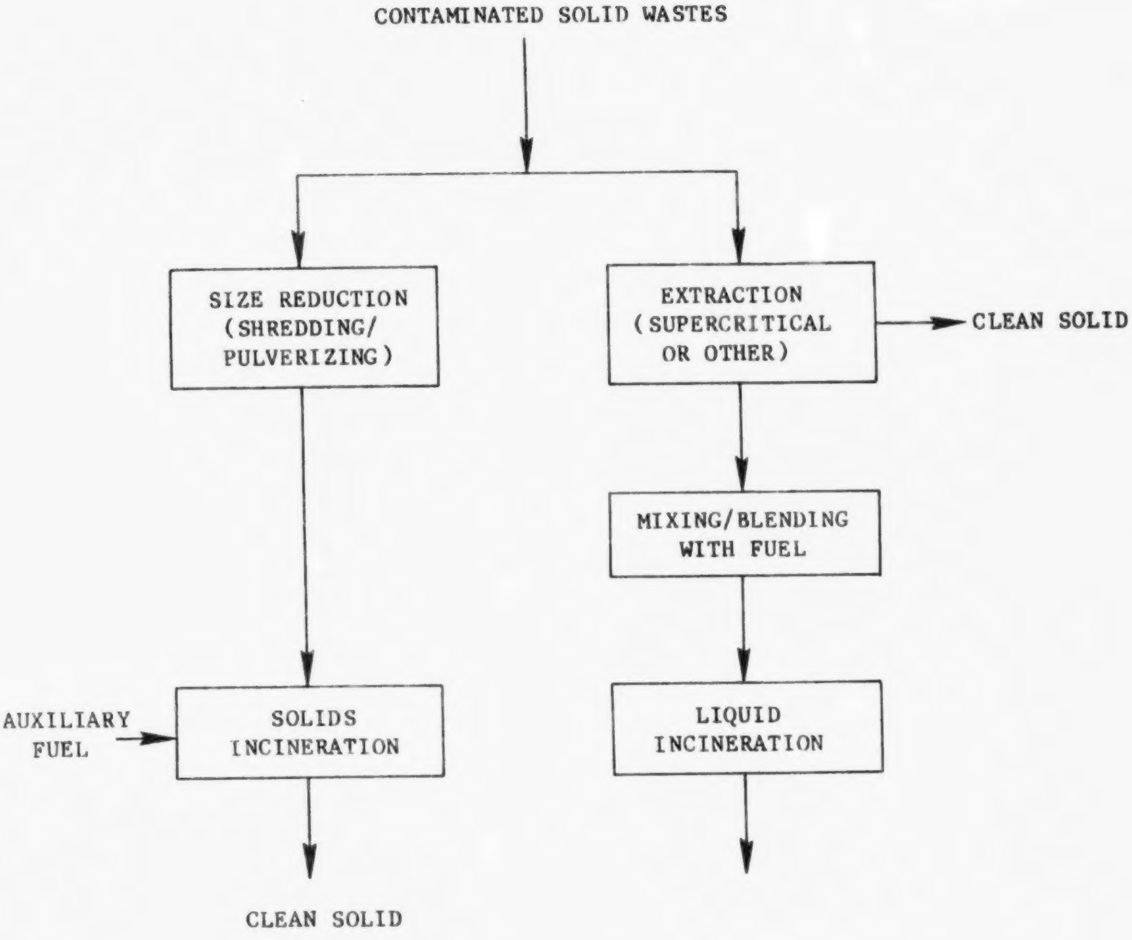
CONTAMINATED SOLID WASTES
SIZE REDUCTION (SHREDDING/ PULVERIZING)
EXTRACTION (SUPERCRITICAL OR OTHER)
CLEAN SOLID
MIXING/BLENDING WITH FUEL
AUXILIARY FUEL
SOLIDS INCINERATION
LIQUID INCINERATION
CLEAN SOLID

Figure 6.3. Alternatives for incinerating contaminated solid wastes.

principle to liquid/liquid extraction (which is discussed later) except that the selection of the extracting solvent may be more critical. Since it is desirable to return the soil to its place of origin, the solvent must be nonhazardous. The EPA Mobile Soils Washing System (MSWS) uses water or water with nontoxic and/or biodegradable additives as the solvent.[8] Another variation to the extraction process is to use supercritical fluids to extract the contaminants. A supercritical fluid is a substance that has been heated above its critical temperature and compressed beyond its critical pressure. Under these conditions fluids generally have greatly increased solute capacities. In addition to water, whose application as a supercritical fluid is discussed later, fluids that have potential in this application include carbon dioxide and ethylene. The use of supercritical ethylene to extract trichlorophenol from soil has been studied at the University of Illinois. Supercritical carbon dioxide has been utilized to remove compounds that have been adsorbed to activated carbon (as an alternative to thermal regeneration).[9] The use of supercritical fluids to extract contaminants from soil and other solids may become a common pretreatment operation in the future.

6.4 BULKY, NON-UNIFORM SOLID WASTES

Contaminated solids can exist in a variety of shapes and forms. Many treatment processes, however, require that solids be of a uniform shape and size in order to be fed to the process. For example, the High Temperature Fluid Wall process requires that solids be free-flowing, non-agglomerating and smaller than 100 mesh (0.0059 inches) in size. Fluidized incinerators generally require that solids be less than 1 inch in diameter. In order to treat large, non-uniform solids with these processes, some type of pretreatment, as indicated in the left-hand side of Figure 6.3, that reduces the size of the solids must be employed. Equipment to reduce size includes shredders, hammermills, and crushers.

6.5 LOW HEAT CONTENT OR HIGH VISCOSITY LIQUIDS

Final treatment of many solvent wastes involves destruction by incineration. Sometimes, when the heating value of the waste solvent is too low, it is possible to blend it with another waste or with fuel to produce a mixture with a heating value high enough to support combustion (> 8000 Btu/lb). Mixing or blending of a waste with another liquid is also sometimes employed to reduce the viscosity of the waste so that it can be atomized. Liquid injection incinerators generally require that the kinematic viscosity of the waste be less than 150 SSU (Standard Saybolt Units) for proper atomization.[10] Preheating or blending of a high viscosity waste with, for example, a number 2 fuel oil (maximum viscosity of 38 SSU at 100°F), are options that could be considered to achieve the viscosity needed for good atomization.

Pretreatment requirements for specific technologies are discussed in following sections.

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SECTION 7.0

PHYSICAL TREATMENT PROCESSES

The treatment processes discussed in this section are based on physical methods of separation and generally do not result in destruction of the contaminants in the waste feed stream. Processes discussed are:

7.1 Distillation

7.2 Evaporation

7.3 Steam Stripping

7.4 Air Stripping

7.5 Liquid-Liquid Extraction

7.6 Carbon Adsorption

7.7 Resin Adsorption

All of these processes are used to some extent for the treatment of wastes, but differ in their applicability to various types of wastes and their need for pretreatment and post-treatment procedures. Evaporation and distillation, for example, are applicable to high organic content wastes but usually generate a large volume residual that contains appreciable organic contamination. Incineration is often the principal means of handling this type of residual. The next three processes, air and steam stripping and liquid-liquid extraction, are applicable to a broad concentration range of contaminants, usually in aqueous media. Air stripping is generally applied to low levels of volatile contamination, steam stripping is suitable for somewhat higher levels of contamination, and liquid extraction possible for both low and high contaminant levels. However, some level of residual contamination requiring additional treatment can often be expected from these technologies. Post-treatment options could be biological treatment or possibly adsorption processes. Carbon and resin adsorption, the last two technologies discussed in the section, are commonly used to remove trace amounts of contaminant to achieve low organic concentration levels. However, in certain cases, particularly when contaminant recovery is advantageous, resin adsorption may be considered for treatment of contaminant levels greater than 0.5 percent, a level above which carbon adsorption may become too costly to be practical. The merits of these processes, including technical performance and costs, must be assessed to select the optimum process or processes. Processes based on chemical and biological treatment and other technologies discussed in following sections must also be considered in arriving at the optimum selection of treatment system components.

The physical treatment processes (and the other treatment processes discussed in following sections) are considered within the framework of four major areas; i.e., (1) Process Description including pre-treatment and post-treatment requirements, (2) Demonstrated Performance in Field and Laboratory, (3) Cost of Treatment, and (4) Overall Status of the Technology. Following discussions of various types of treatment processes applicable to solvent and other low molecular weight organics (Sections 7.0 through 13.0), a review section (Section 14.0) is provided that addresses possible approaches to identifying potential treatment processes or combination of processes that is likely to meet treatment requirements in the most cost effective manner.

7.1 DISTILLATION

7.1.1 Process Description

Distillation can be broadly described as a separation technique that operates on the principle of differential volatility. More volatile constituents can be enriched or separated by heating and volatilizing from less volatile constituents. Most distillation systems fall into one of four general categories.

1. Batch distillation;
2. Continuous distillation;
3. Batch fractionation; and
4. Continuous fractionation.

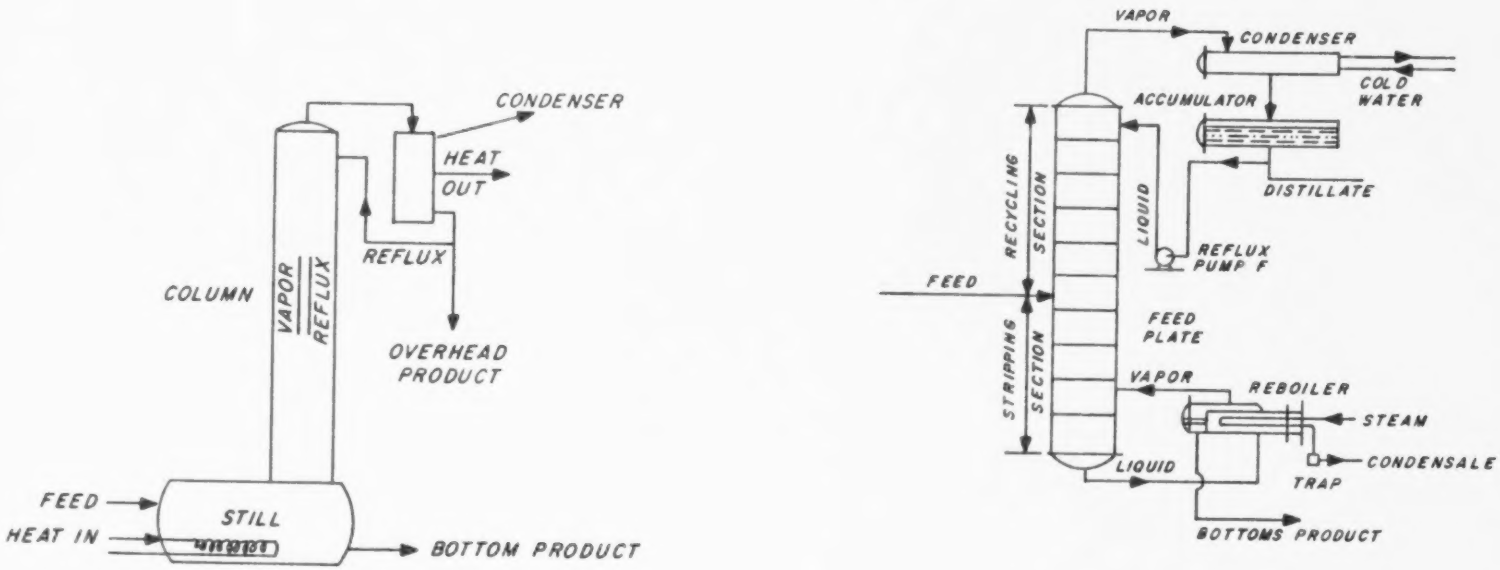
In batch distillation, the system is charged with a given quantity of waste solvent and heated indirectly with steam or oil, with coils or the vessel wall acting as the heat transfer surface. Heating continues until a predetermined fraction of the volatile components is removed, as indicated by the time/temperature profile of the charge within the still. At this point heating is discontinued and the bottom product or less volatile residues removed. The disposal of these residues will be limited by their characteristics. In many cases, it will be expeditious to maintain a residue that can be handled readily and that can be incinerated, i.e., that is pumpable and has Btu value. In any event, it must be recognized that complete removal of volatiles will not be feasible. Attempts to reduce solvent content to low levels can result in compound destruction and equipment fouling. Solvent removal efficiencies must balance the benefits of recovery against the costs of equipment maintenance and the cost and manner of residual disposal.

Continuous distillation functions much the same as batch distillation, except the waste solvent is charged continuously, resulting in steady-state operation. Removal of the bottoms product can take place continuously or it may be batch removed at specific intervals. Continuous bottoms removal generally implies that the stream is pumpable. In response to economic incentives to recycle and minimize wastes, several small stills have been introduced to the solvent recovery market which permit close to complete recovery as a result of design features such as removable liners for bottoms disposal. Many can be operated either continuously or by batch mode and under vacuum to effect even greater recovery.

The separation of solvent mixtures requires multiple distillations or fractionation since adequate separation of fluids with similar boiling ranges is not achieved in a single stage. Fractionation column designs include the use of multiple trays or packing to maximize surface area so that rising vapors are intimately contacted with falling condensate (reflux). These columns can be operated as batch or continuous units. Figure 7.1.1 shows basic process schematics for batch and continuous fractionation systems.[1]

Fractional distillation is a very well developed industrial technology that has been studied extensively for many years, particularly by the petrochemical industry. Vapor-liquid equilibrium data provide the basis for evaluating the feasibility of fractionation. A McCabe-Thiele diagram, which graphically illustrates the fractionation process, is shown in Figure 7.1.2.[2] The figure shows the minimum number of theoretical column stages required to effect separation; i.e., 100 percent efficiency at total reflux. Detailed discussions of fractional distillation theory and practice, including the use of well-developed models for predicting separation, can be found in chemical engineering texts and in Perry's Chemical Engineers' Handbook.

In continuous fractionation, feed is constantly charged to the column at a point which provides the specified top and bottoms product. The section of the tower above the feed point is the rectifying or enriching section, and the section below the feed point is the stripping section. A reboiler is connected to the bottom of the fractionation tower to provide the reboil heat needed for added reflux and better fractionation of complex mixtures. Batch fractionation differs in that the charge is introduced at the bottom of the tower. Consequently, it is possible to obtain a distillate of high purity, but recovery of the less volatile component(s) must proceed in a step-wise manner. As the more volatile solvent is taken off, the reflux and



BATCH FRACTIONATION

CONTINUOUS FRACTIONATION

Figure 7.1.1. Basic schematic for batch and continuous fractionation systems.

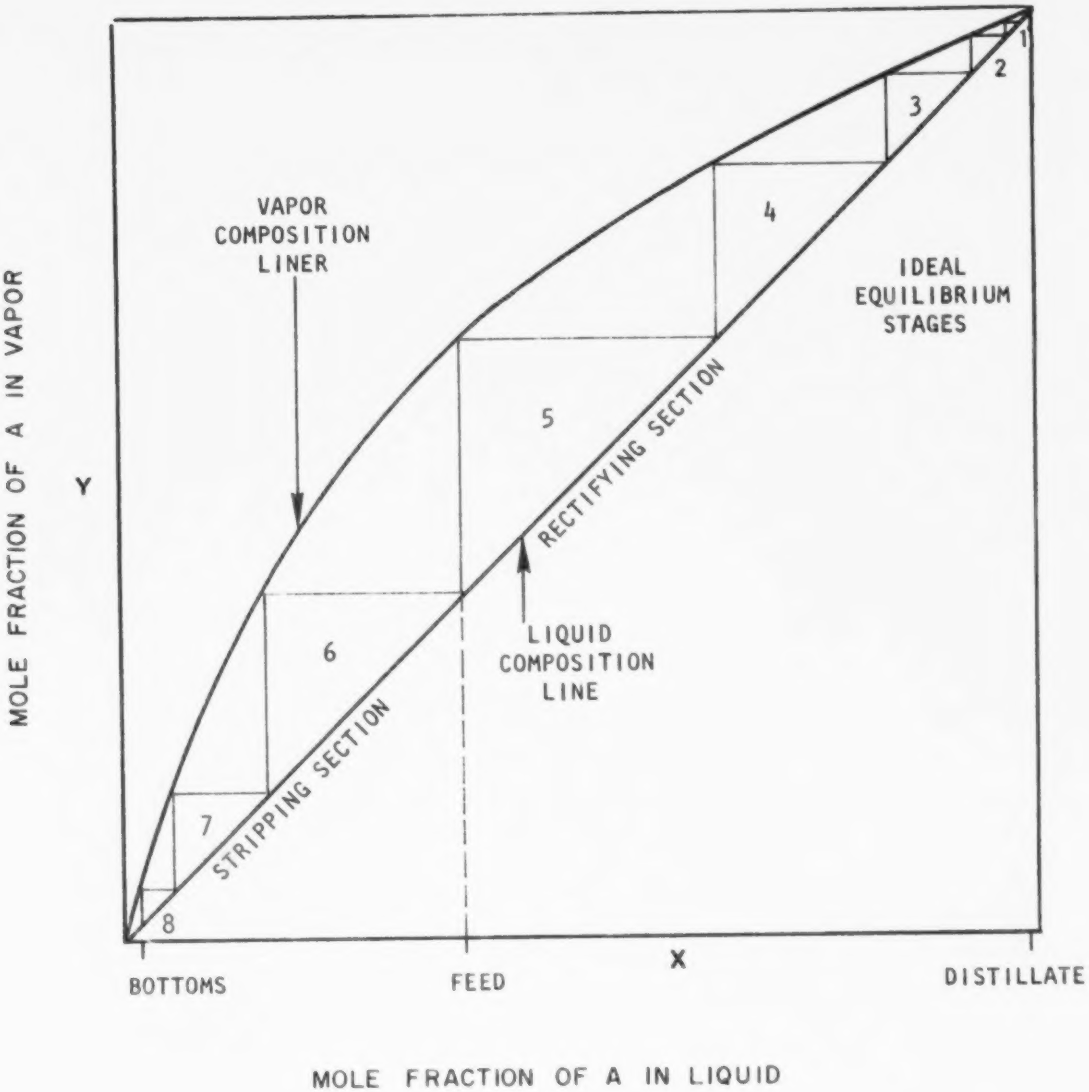


Figure 7.1.2. McCabe-Thiele diagram for distillation. (Total reflux = no products taken off.)

thus, energy consumption, must be increased to maintain overhead product purity. At some point, the overhead quality decreases to the point where it must be removed and stored separately until the less volatile component(s) is enriched enough to generate a useful product. However, batch fractionation does permit handling of wastes with higher dissolved solids content which would foul the stripping zone surfaces in a continuous feed column.

7.1.1.1 Restrictive Waste Characteristics--

Batch Distillation

Batch distillation equipment has undergone considerable development in recent years, particularly that of interest to the small quantity generator. Almost any solvent waste can be processed in commercially available equipment, including high solids, ignitable and potentially explosive mixtures. However, there are some restrictions which affect safety and product purity that should be considered.

Typically, the boiler temperature is set at 20°F to 30°F higher than the boiling point of the solvent to ensure vaporization. Highly contaminated solvents (i.e., high solids) and mixtures which form high boiling azeotropes would require higher temperatures to effect separation. However, the temperature of the still must remain below (20 to 30°F) the autoignition point of the solvent. Thus, at least 40°C between autoignition point and boiling point is required for distillation of high purity mixtures. Autoignition temperatures for most solvents can be found in the National Fire Protection Association's "Fire Protection Guide for Hazardous Materials".[3] Heptane is generally considered to have the lowest autoignition point (399°F) of commonly recovered solvents.[4] For this reason (to minimize risk of explosion), many manufacturers design units which are limited to a maximum temperature of 365°F.

Many small stills are explosion proof, but the potential for explosion should be evaluated, especially for solvent mixtures. Autoignition temperatures of ignitable wastes may pose particular handling problems in distillation units since some of the particular solvents addressed in this document have even lower autoignition points than does heptane. Table 7.1.1 gives examples of some of these. It should be noted that there are several other constituents not addressed by this document that exhibit even lower autoignition points (see Reference 3).

Most halogenated solvents are nonflammable but are susceptible to thermal decay. Thermal decay occurs at low temperatures relative to autoignition points. For low autoignition point and low decomposition temperature solvents, vacuum operation is an option that is available in many of the currently marketed batch stills. Additional expenses, capital and operating, are at least partially offset by the reduced boiling temperature and higher potential recovery rates.

Solids content, which is a critical limitation for continuous distillation and fractionation processes is less critical for batch distillation or continuous feed with batch bottoms removal. In particular, jacketed and immersion heated boilers with provisions for easy bottoms removal are capable of achieving high recovery rates. Residual solvents remain in the bottoms produced from these operations, but potential recoveries are usually greater than 90 percent regardless of initial solid constituent concentration. In many cases, the distillation occurs over a long enough period of time such that potentially reduced mass diffusion and heat transfer do not greatly reduce the overall effectiveness of the recovery process.

Continuous Distillation

Continuous distillation is subject to the same constraints that apply to batch distillation in terms of operating temperature. However, the distinction between batch and continuous bottoms removal greatly effects the applicability and achievable performance for certain waste types.

Continuous feed, batch bottoms removal units are essentially the same as batch units in terms of processing capabilities. Continuous feed units have greater capital costs since they do require some additional control features (i.e., level control), but are more automated thereby requiring less labor. These units are preferred for high throughput applications where labor costs become a higher fraction of total costs than capital equipment costs.

TABLE 7.1.1. BOILING POINTS AND AUTOIGNITION POINTS OF RISK SOLVENTS

Solvent	Autoignition Point(°F)	Boiling Point(°F)
acrolein	428	125
ethanol	347	70
ethyl ether	356	95
1,3-dioxane	356	214
heptane	399	209

Source: Reference 3.

The continuous feed, continuous bottoms removal units are different in that the achievable recovery is controlled by the ultimate disposition of the bottoms. Continuous bottoms removal implies the bottoms remain fluid. In cases where bottoms become highly viscous, ultimate recovery is limited by equipment processing constraints. These materials are more optimally processed in thin-film evaporators which are capable of achieving high recovery rates and throughputs in a shorter period of time (see Section 7.2). Scraped-surface stills also increase the ultimate recovery but by a smaller amount. Thus, continuous bottoms recovery stills are best suited to recovering spent solvents which produce residual bottoms that are non-fouling and that remain pumpable after separation.

Batch Fractionation

Fractionation is a multi-stage process used for separating solvent mixtures when the value of the pure component products justifies the additional expenses associated with separation. Pure components can be sold for 80 to 90 percent of the virgin price whereas solvent blends typically sell for only 50 to 60 percent of virgin prices.[5] As with batch distillation, batch fractionation can handle a higher solids content waste form since these materials do not come into contact with the packing or trays. The quantity and nature of the solids in the waste may become a limitation depending upon the design of the heat transfer unit. Excessive fouling may interfere with heat transfer requiring higher energy costs, reduced throughput, and additional labor. Agitated units are available to reduce the potential problems due to fouling.

Continuous Fractionation

As opposed to batch fractionation, continuous fractionation is reserved for materials which are essentially void of dissolved and suspended solids. The feed enters at a mid-point in the column where it comes into intimate contact with tray or packing surfaces. Labor costs associated with cleaning these units justify pretreatment in either a distillation or evaporation unit. Also, the bottoms product will have to be treated to remove the nonvolatile constituents.

Azeotrope Formation

Two limiting characteristics of a waste stream effect the application of both batch and continuous fractionation. As described for batch distillation, temperature limits must be considered for constituents with low autoignition and thermal decomposition limits. A second potential separation problem arises with the formation of azeotropes when, at a certain limiting solvent concentration, two or more constituents have the same relative volatility, making further enrichment impossible.

Table 7.1.2 provides a list of water/solvent azeotropes with azeotropic and pure component boiling points and overhead product composition. All of the systems shown form low boiling azeotropes with water, with nonmiscible compounds separating into two phases as indicated. Table 7.1.3 provides further data on multicomponent organic systems that form tertiary and quaternary azeotropes with water. Additional azeotrope data can be found in the literature. Minimum boiling azeotropes represent the limiting concentration obtainable in an overhead product unless the azeotrope is disrupted through the addition of another constituent, e.g., extractive distillation. This is discussed further in Section 7.2. In certain cases , azeotropes may not occur, but relative composition differences between the liquid and vapor phase might be so small as to render the separation economically unfeasible. The vapor-liquid equilibrium (VLE)data must be evaluated for separational feasibility. The McCabe-Thiele diagram (Figure 7.1.2) is based on VLE data. It is evident that if the vapor and liquid composition lines are close enough, many equilibrium stages might be required.

7.1.1.2 Operating Parameters and Design Criteria--

Distillation and fractionation processes are based on the evaporation and condensing of constituents. Operating parameters of critical importance for all units are process temperature and process pressure. Higher operating pressures are routinely used for low boiling constituents to avoid the use of energy intensive refrigeration to achieve condensation. This is particularly true for fractionation processes which requires greater reboiler and condenser

TABLE 7.1.2. AZEOTROPE FORMATION OF COMPOUNDS WITH WATER

	Pure compound boiling point (C°)	Azeotropic boiling point (C°)	Percent composition			Relative Volume (%)	
			Total	Upper layer	Lower layer	Upper layer	Lower layer
Solvents of Concern							
1,1,2-Trichloro-1,2,2-trifluoroethane	47.7	44.5	99.0	1.0	99.9	2.0	98.0
1-Butanol (I)	117.7	93.0	55.5	79.9	7.7	-	-
Carbon disulfide	46.3	43.6	98.0	0.29	99.99	2.3	97.7
Carbon tetrachloride	76.8	66.3	95.9	0.03	99.97	6.4	93.6
Chlorobenzene	132	90.2	71.6	-	-	-	-
Cyclohexanone (I)	155.4	95	38.4	92.0	2.3	41.5	58.5
Ethyl acetate (I)	77.2	70.4	91.9	96.7	8.7	95.0	5.0
Ethyl ether (I)	36.4	34.2	98.8	-	-	-	-
Ethylbenzene	136.2	92.0	67.0	99.95	0.02	70.0	30.0
Isobutyl alcohol (I,T)	108.4	89.7	70.0	85.0	8.7	82.3	17.7
Methanol (I)	64.7	-	-	-	-	-	-
Methyl ethyl ketone (I,T)	79.6	73.4	88.0	-	-	-	-
Methyl isobutyl ketone (I)	115.1	87.9	76.0	98.4	2.0	80.4	19.6
Methylene chloride	40.0	38.8	99.0	2.0	99.9	1.6	98.4
Pyridine	115.5	92.6	57.0	-	-	-	-
Tetrachloroethylene	121.0	88.5	82.8	0.02	99.9	25.0	75.0
Toluene	110.6	85.0	79.8	99.95	0.06	82.0	18.0
Xylene (I)	139.1	94.5	60.0	99.95	0.05	63.4	36.6
Other Organics							
1,1,2-Trichloroethane	113.7	86.0	83.6	0.45	99.95	22.0	78.0
1,1-Dichloroethylene	83.5	71.6	92.0	0.08	99.8	-	-
1,4-Dichloro-2-butene (I,T)	101.3	87.8	81.6	-	-	-	-
2-Ethoxy ethanol	135.1	99.4	28.8	-	-	-	-
2-Nitropropane (I)	120.25	88.55	70.6	-	-	-	-
Acetonitrile (I,T)	82.0	76.5	83.7	-	-	-	-
Benzene (I,T)	80.1	69.4	91.1	99.94	0.007	92.0	8.0
Chloroform	61.2	56.1	97.0	0.8	99.8	4.4	95.6
Cyclohexane (I)	81.4	69.8	91.5	99.99	0.01	93.2	6.8
Ethylene dichloride	84.0	71.6	91.8	0.8	99.8	10	90
Furfural (I)	161.5	97.5	35	-	-	-	-
Acrolein	52.5	52.4	97.4	-	-	-	-
Allyl alcohol	97.1	88.2	72.9	-	-	-	-
Allyl chloride	44.9	43.0	97.8	-	-	-	-
Epichlorohydrin	117.0	88.5	74.0	5.9	98.8	30.0	70.0
Ethyl acrylate (I)	99.8	81.0	84.9	98.5	2.0	87.0	13.0
Ethylene diamine	116.5	119.0	81.6	-	-	-	-
Paraldehyde	124.5	90.8	74.8	98.9	10.5	73.0	27.0

Sources: References 2, 6, 7, 8

TABLE 7.1.3. SAMPLE DATA ON AZEOTROPE FORMATION

Binaries			
A	B	bp°C	%A
Methylene Chloride	Methanol	37.8	92.7
	Ethanol	39.9	95
	Dichlorobenzene	171.3	48
Methanol	1,1,1-Trichloroethane	56	21.7
	Acetone	55.5	12
	Methyl Acetate	54	19.5
	Ethyl Acetate	62.3	44
	MEK	64.5	70
Perchloroethylene	Ethanol	76.7	37
Ethanol	Methyl Acetate	56.9	3
	Ethyl Acetate	71.8	31
	Toluene	76.7	68
	Heptane	70.9	49
	Benzene	67.9	31.7
Acetone	Methyl Acetate	56	50
	Heptane	55.8	89.5
Carbon Tetrachloride	Ethyl Alcohol	65	84
	MEK	50	84.3
		73.7	81.6
	Ethyl Acetate	74.8	57

Tertiaries				Percent		
A	B	C	bp°C	A	B	C
Water	Ethanol	Ethyl Acetate	70.3	9	8.4	82.6
	Ethanol	Benzene	74.1	7.4	18.5	74.1
	Ethanol	MEK	73.2	11	14	75
	Ethanol	Toluene	74.4	12	37	51
Methanol	Acetone	Hexane	47	14.6	30.8	59.6

Quarternaries					Percent			
A	B	C	D	bp°C	A	B	C	D
Water	Ethanol	Benzene	Cyclohexane	62.2	7.1	17.4	21.5	54
Water	Butyl Alcohol	Butyl Acetate	Butyl Ether	90.6	30	13	51	6

Source: Reference No. 5

duties as a result of occurring reflux. Distillation units, particularly small batch units capable of processing up to 60 gallons per hour, are often equipped with vacuum capability. High temperatures combined with low pressure makes high recoveries possible, even for high boiling constituents.

Other parameters that must be considered include batch time, viscosity (flow and mass transfer), reflux ratio, and the location of feed introduction to the column. Batch time is chosen based on economics, desired recovery, and restrictive waste characteristics. Certain units may be susceptible to fouling problems or viscosity problems. High viscosity wastes are best treated in agitated thin-film evaporators (see Section 7.2).

Reflux rate and feed tray location are process variables strictly applicable to fractionation, with feed tray designation applicable specifically to continuous distillation. Reflux rate or ratio is set based on the economic evaluation of product purity versus utility costs. High reflux ratios produce higher purity products but are more energy intensive. In addition, the high internal flow rates often establish the need for either larger units, or lower throughputs. Optimal feed location in a column will be at the point of intersection of the rectifying and stripping operating lines.[2]

In reference to these process considerations and other design criteria, Custom Organics, Inc. compared batch and continuous fractionation based on experience in the production of specialty organic products.[9] The advantages of continuous fractionation were stated as follows:

1. A continuous fractionating column has both a rectifying section in which the low boiling point component is being enriched and a stripping section in which the higher boiling component is being enriched. The available trays are more effective in this configuration than as a single rectifying section.

2. Increased separation efficiency for continuous fractionation is best achieved through increasing the number of trays. In a batch still the most effective way of improving the separation is to increase the reflux ratio which reduces production capacity and energy efficiency.

3. The rate of separation of components is greater in a continuous still than in a batch still.

4. Liquid holdup volume is not a factor in the design of a continuous fractionating process because the temperature/composition profile is constant. In batch columns, the holdup volume critically affects the column efficiency.

5. Constant operating conditions enable predicted performance of continuous fractionation units to be determined with some degree of accuracy. Conversely, mathematical models for batch units are complex and less exact.

6. Optimization of a continuous distillation column involves a fairly simple balance between product quality and increased operating costs associated with a higher reflux ratio. A batch column requires a trade-off for optimum operation between a constant reflux ratio and a constant overhead product composition.

7. Because the composition of all streams is fixed in continuous fractionation, it is easier to plan and manage process and quality control.

8. The flexibility of changing the feed and take off trays with continuous column make continuous fractionation a very powerful separation technique. Any tray in the column can be used for feed or product withdrawal, and it is not unusual to have three product streams withdrawn simultaneously. In contrast, the only product from a batch unit is distillate. It is more difficult to seperate multicomponent vapor streams due to continually changing concentrations.

9. Short product residence time makes continuous fractionation very much superior to batch for temperature sensitive materials.

10. The time required for handling or housekeeping operations is minimal for continuous relative to batch fractionation.

However, continuous fractionation has several disadvantages. It requires considerably more skill to operate than batch systems. Batch distillation is also capable of handling wastes with suspended or dissolved solids without prior evaporative treatment. In addition, it not always possible to remove products as desired from a multicomponent waste in a continuous column. Batch processing offers the capability of recovering different products at different times when potentially more than one column may be required for a continuous process. Another potential limitation of continuous fractionation is the effect of inconsistent feed composition. The continuous column is sensitive to change, and a change in feed composition could upset steady-state operation and adversely impact product quality.

As mentioned previously, fractionating towers can be either a packed tower or tray (plate) tower. The choice between use of plate or packed tower should be based on a cost analysis. In many cases, however, the decision can be made by a qualitative analysis of the advantage and disadvantages eliminating a detailed cost comparison. The following summarizes the advantages and disadvantages of plate versus packed towers as presented by Peters and Timmerhaus in Plant Design and Economics for Chemical Engineers.[10]

- Stage efficiencies for packed towers must be based on experimental tests with each type of packing.
- The design of plate columns is more reliable as a result of liquid dispersion difficulties in packed columns, especially for the case at a low liquid to vapor flow ratio.
- Plate towers can be designed to handle wide ranges of liquid rates without flooding.
- Plates are more accessible for cleaning.
- Plate towers are preferred if interstage cooling is required. Cooling coils can be installed on the plates or the liquid-delivery line from plate to plate can be passed through an external cooler.
- Distillation packing may be crushed by thermal expansion or contraction brought on by large temperature changes.
- Random-packed towers are seldom designed with diameters larger than 4 ft, and diameters of commercial plate towers are seldom less than 2 ft.
- Packed towers are usually preferred if the liquids have a large tendency to foam.
- The amount of liquid holdup is considerably less in packed towers.
- The pressure drop through packed towers may be less than the pressure drop through plate towers designed for the same duty. This advantage, plus the fact that the packing serves to lessen the possibility of tower-wall collapse, makes packed towers particularly desirable for vacuum operation.

In a report provided for EPA, the Water General Corporation summarized the performance of packing and different tray types as presented in Tables 7.1.4 and 7.1.5.[11]

7.1.1.3 Treatment Combinations--

For distillation, pretreatment options consist of filtration, centrifugation and other physical means (see Section 6) to separate solids from the liquid stream and decanting to separate gross sediment and immiscible fluids.

Post treatment methods used for overhead product include further refinement through separation of mixtures into its pure components. This is performed to enhance the value of the recovered solvent or to meet product purity specifications. Fractionation is usually performed on spent solvents which have already been separated from nonvolatile constituents. It is also a typical regeneration technique for solvent used in solvent extraction. In cases where the distillate product consists of two phases, decanting is a typical post-treatment procedure. If water is soluble in the solvent to an extent which exceeds product purity specifications (e.g., methylene chloride), the solvent stream will undergo some form of drying to remove the water. Commonly employed drying methods include molecular sieve, calcium chloride, ionic resin adsorption, and caustic extraction.

Post treatment options for bottoms products depend on the physical form of the material. Approximately two-thirds of recycled solvent bottoms generated by commercial recyclers are used as is or blended with higher Btu products for use as a fuel (Section 3.2). For solvent blends containing expensive halogenated constituents, there are cases where liquids are added prior to distillation to promote maximum removal of the halogenated constituents by keeping the bottoms fluid. Other treatment options consist of further solid-liquid separation for organic liquids and sludges, organic removal or extraction processes for aqueous wastes, and thermal destruction techniques.

Solid-liquid separations can be accomplished by physical means such as centrifugation, filtration, decanting and extraction. Dilute aqueous wastes can be treated through air or steam stripping, carbon or resin adsorption, or biological treatment as described in other sections.

TABLE 7.1.4. RELATIVE PERFORMANCE RATINGS OF TRAYS AND PACKINGS*

Parameter	Trays			Packings	
	bubble cap	sieve	valve	high void	normal
Vapor capacity	3	4	4	5	2
Liquid capacity	4	4	4	5	3
Efficiency	3	4	4	5	2
Flexibility	5	3	5	2	2
Pressure drop	3	4	4	5	2
Cost	3	5	4	1	3

*5 = excellent; 4 = very good; 3 = good; 2 = fair; 1 = poor.
Source: Reference 11.

TABLE 7.1.5. SELECTION GUIDE FOR TOWER INTERNALS*

Parameter	Trays		Packings	
	bubble cap	sieve or valve	random	stacked
Pressure, low	1	2	2	3
moderate	2	3	2	1
high	2	3	2	0
High turndown ratio	3	2	1	2
Low liquid flow rates	3	1	1	2
Foaming systems	1	2	3	0
Internal tower cooling	3	2	1	0
Suspended solids	1	2	1	0
Dirty or polymerized solutions	1	2	1	0
Multiple feeds or sidestreams	3	3	1	0
High liquid flow rates	1	2	3	0
Small diameter columns	1	1	3	2
Column diameter 1 to 3 m	2	3	2	2
Larger diameter columns	1	3	2	1
Corrosive fluids	1	2	3	1
Viscous fluids	1	2	3	0
Low pressure drop	0	1	2	3
Expanded column capacity	0	2	2	3
Low cost	1	2	2	1
Reliability of design	2	3	2	1

*0 = do not use; 1 = evaluate carefully; 2 = usually applicable;
3 = best selection.
Source: Reference 11.

7.1.2 Demonstrated Performance

A number of studies have been conducted demonstrating the feasibility of solvent recovery by distillation processes. Although residual solvent concentrations in treated wastes were always high enough to require additional treatment, all these studies demonstrated significant economic benefits similar to those shown previously in Section 5. The cost benefits of the studies discussed below will be discussed in detail in Section 7.1.3.

3M Company: Packaged Batch Distillation Units, Reference 12

Small batch distillation units for recovery of solvents from low volume wet scrap were evaluated by the 3M Company in 1984.[12] Many of the wastes were described as nonpumpable in nature, which limited the options for recovering the solvents to small batch stills. Units built by Zerpa Industries and the Finish Engineering Company were evaluated for three different applications, as shown in Table 7.1.6. Table 7.1.6 also summarizes the achieved recovery rates and stream compositions.

Application 1:

Application No. 1 involved the recovery of 1,1,1-trichloroethane (1,1,1-TCE) from degreasing scrap. The scrap contained 84.1 percent 1,1,1-TCE, 6.4 percent oil and grease, 6.6 percent total solids, and 2.9 percent unidentified inhibitors which act as stabilizers for 1,1,1-TCE.

This scrap responded well to distillation resulting in an overhead rich in low boilers (160 to 178°F boiling point range of 1,1,1-TCE and inhibitors) and bottoms product rich in high boilers (300°F for these oils) and nonvolatiles (solids). Batch distillation of 2 gallons per hour of scrap at 290°F resulted in 99 percent solvent recovery. The overhead was clear, and contained 95 percent 1,1,1-TCE, 0.02 percent oil and grease, 0.02 percent total solids, and a 4.96 percent unidentified component which was believed to consist of the inhibitor system. Twelve percent of the feed weight was recovered as a bottoms product. This consisted of a solid cake residue containing freely drainable oil and 8.2 percent by weight 1,1,1-TCE.

TABLE 7.1.6. SMALL STILL PERFORMANCE EVALUATION

Application 1: Recovery: 99%. Separation of Low and High Boilers

Stream	Composition (%)				
	1,1,1-trichloroethane	Oil/grease	Solid	Inhibitors	Comments
waste feed	84.1	6.4	6.6	2.9	---
distillate	95	0.02	0.02	4.96	clear
bottoms	8.2	NR	NR	NR	---

NR: Not Reported

Application 2: Recovery: 76%. Processing High Viscosity and High Solids Scrap

Stream	Composition (%)		
	Solvent	Solid	Comments
waste feed	79.0[a]	21.0	---
distillate	99.9	0.002	clear
bottoms	[b]	NR	elastic cake

[a] mostly heptane/remainder naphthones and other paraffins (BP 190-219°F)

[b] subjected to EPA leach test: leachate contained 43ppm heptane

Application 3: Recovery: 97.4%. Processing Solvent Contaminated Refuse

Stream	Composition (%)			
	MEK/Toluene	Other Solvents	Solid	Comments
waste feed	48.0	13	39	---
distillate	(-----------99.99--------------)		0.01	clear
bottoms	(-------------4----------------)[a]		96	hard conglomerate

[a] subjected to EPA leach test: leachate contained 2ppm MEK, 1.7ppm toluene, 900ppm unidentified

Source: Reference 12.

The economics of using a wet scrap processing are attractive, with investment payback period estimated to be 4 months, after considering credit for reclaimed solvent and reductions in waste transportation and disposal costs.

Application 2:

Application No. 2 involved processing a difficult-to-treat, highly viscous (10,000 cp) adhesive scrap containing heptane and other solvents (79 percent) and high solids content (21 percent). Previous attempts were made within 3M to recover solvent from this scrap through spray drying and thin film evaporation. Spray drying failed when the processed scrap became tacky and plugged the dryer. Thin film evaporation was successful, but was not economical due to the low volume of waste generated (44,400 gal.yr).

Distillation of this scrap produced an overhead rich in low boilers including heptane, naphthenes and other parafins (190 through 219°F boiling point range) and a bottoms product consisting mainly of nonvolatiles (solids). Batch distillation of 2.7 gal/hr of scrap at 350°F resulted in 76 percent solvent recovery. The overhead was clear and contained 99.9 percent solvent and 0.002 percent total nonvolatiles. Forty percent of the feed weight was recovered as bottoms product. This product resembled a nonflowable elastic cake and contained 55 percent solvent. The bottoms product was subjected to the standard EPA leach test. The leachate contained 43 ppm heptane and 1 ppm of another material that was unidentified.

The economics of using a wet scrap processing still were judged to be favorable with the investment payback period estimated to be 17 months.

Application 3:

Application No. 3 involved processing solvent contaminated industrial refuse which primarily consisted of low-density rags and filter cartridges. This scrap required wet scrap processing units with larger distillation chambers relative to previous tests. The nature of this scrap (high solids content and low packing density) was expected to result in poor heat transfer, long processing times, and a wet bottoms product but these problems did not materialize.

The scrap tested contained 61 percent solvent and 39 percent solids. MEK and toluene accounted for 48 percent of the feed weight. Distillation of this scrap produced an overhead rich in low boilers and a bottoms product consisting of nonvolatiles (solids). Batch distillation of 3.4 gal/hr of scrap at 350°F resulted in 97.4 percent solvent recovery. The overhead was clear and contained 99.99 percent solvent and 0.01 percent solids. Forty-one percent of the waste was recovered as bottoms product, which was a hard conglomerate of dried rags and filter cartridges. Four percent of this bottoms product's weight was solvent. The bottoms product was subjected to the standard EPA leach test. The leachate contained 2 ppm MEK, 1.7 ppm toluene, and 900 ppm unidentified material.

The economics of using a wet scrap processing still are promising . The estimated investment payback period was 6 months.

GCA: Package Batch Distillation Unit

GCA, under contract to EPA, evaluated the performance of a Zerpa RX-35 Recyclene still used for the reclamation of spent solvent used as a printed circuit board developer.[13] The application involved the recovery of 1,1,1-trichloroethane (1,1,1-TCE) contaminated with undeveloped photoresist (a 100 percent organic thermoplastic polymer consisting of acrylic monomers and polymers and small quantities of chlorine substituted nitro heterocycles). The spent developing solution, concentrated through a previous batch distillation process using a Dupont-Riston SRS-120 unit, consisted of 88 percent 1,1,1-TCE, 2 percent solids, and 10 percent breakdown products and additives. A 25 gallon charge distilled at 350°F for 2 hours in the Zerpa still resulted in 99.9 percent solvent recovery. The overhead was contaminated with less than 0.001 percent total solids and was suitable for reuse in the developer. The bottoms consisted of a dry solid residue containing 7.5 percent 1,1,1-TCE and 1 percent breadkown products and additives (see Table 7.1.7). The unit was able to achieve a 6 month payback.

TABLE 7.1.7. SUMMARY: GCA/OSW CASE STUDY

Recovery: 99%. Recycling Photoresist Solvent

Stream	Composition (wt %)		
	1,1,1-trichloroethane	solid	other
waste feed	88.0	2.0	10.0
distillate	8.0	0.001	12.0
bottoms	7.5	91.5	10.1

Source: Reference 13.

GCA: Batch Fractionation Process

GCA conducted a waste minimization study for EPA in 1986 involving a batch fractionation process used for solvent recovery at a printed circuit board and semiconductor manufacturing firm. The solvent was a methyl chloroform and Freon TF (trichlorotriflouroethane) mixture. The Freon and methyl chloroform are used to preclean substrate semiconductor chips and develop photoresist, respectively, producing a waste which typically contains up to 10 percent methyl chloroform and 90 percent Freon.

The waste is distilled in a stainless steel mesh packed column. The tower is 28 feet tall and 12 inches in diameter. Waste solvent is automatically fed from a 1,500 gallon holding tank to a 1,450 gallon batch pot using level controllers in the batch pot. The pot is equipped with a reboiler which heats the solvent mixture to 133°F. Other process parameters are reported in Table 7.1.8.

As the distillation proceeds, the concentration of methyl chloroform in the batch tank increases from an initial concentration of 10 percent in the waste feed to 80 percent after 11 to 13 days. Upon reaching 80 percent, the still bottoms are removed for further processing. Analytical results from samples obtained during the site visit are provided in Table 7.1.9. These data were collected after 6 days of processing which is the reason for the relatively low bottoms concentration.

TABLE 7.1.8. METHYL CHLOROFORM/FREON BATCH DISTILLATION SYSTEM OPERATING INFORMATION

Normal Operating Parameters	
1. Solvent	
Recovery Rate	33 gal/hr
Reboiler Temperature	133°F
Distillate Temperature	75°F
2. Cooling Water	
Flow	72 gal/min
Temperature	47°F
3. Steam	
Flow	470 lbs/hr
4. Electrical Requirements	30 hp

Source: Reference 13.

TABLE 7.1.9. DISTILLATION COLUMN RESULTS

Parameter	Influent	Recovered product	Still bottoms	Virgin Freon TF
Volatile Organics (% w/w)				
- Freon TF	96.1	99.1	51.5	99.99
- Methyl Chloroform	3.9	0.9	47.5	0.01
- Other	0.1	0.1	0.1	0.01
Solids (mg/kg)	1.2	0.06	27	0.13

Source: Reference 13.

The column is operated continuously and is capable of handling up to 1,200 gallons per hour. Approximately 40 million pounds of solvent were processed in 1984, with estimated savings in excess of $8 million.

CH2M Hill: Batch Packaged Stills[14].

CH2M Hill evaluated 18 case studies of waste recycling and minimization for the DOD Environmental Leadership Project and the U.S. Army Corps of Engineers, some of which provided economic justification for various solvent distillation processes. A study of a solvent recycle program at Robins AFB is described below.

Robins AFB operates a batch, atmospheric pressure still ($48,000 purchase price) manufactured by Finish Engineering Corporation which was used to reclaim trichloroethane, Freon-113 (trichlorotriflouroethane), and isopropanol. A facility engineer estimated that in 1984 the recycling of these three chemicals saved the base $118,000 in virgin material and hazardous waste disposal costs. Recovery costs were $13 per drum, whereas disposal of the chemicals and repurchase of new materials would have cost from $250 to $500 per drum.

The organic fluid recovery system consists of a single-stage batch still, a solvent/water separator, and an electrically powered steam generator. The still can operate up to a boiler temperature of 300°F and can reclaim organic fluids at a rate of up to 55 gallons per hour. Freon and isopropanol were processed at a rate of approximately 50 gallons per hour and trichloroethane was processed at a rate of 35 to 40 gallons per hour. Recovery efficiency for isopropanol and Freon-113 is approximately 95 percent. The recovery efficiency for trichloroethane is only 70 percent since the used material contains nonvolatile waxes, dirt, and greases that are removed from metal parts during degreasing operations.

The recovered Freon does not meet Type I military specifications; however, it does meet Type II military specifications and is consequently used for initial cleaning. Virgin solvent is required for final cleaning operations that require Type I Freon. Approximately 175 drums per year of trichloroethane were being reclaimed. Laboratory tests indicate that the recovered trichloroethane meets military specifications and that reclaimed isoproponal is 99.8 percent pure. A 5 micron filter, installed at the condenser outlet to remove fine metal particles carried over with the vapor, was found to enhance recovered product purity.

Robins AFB recently purchased a second still from Finish Engineering for $97,000 to supplement their existing unit. Operating under vacuum, this new system will have the capability of distilling organic fluids that have atmospheric boiling points of up to 500°F while maintaining a 300°F limit in the boiler pot. This new still is to be used to recover materials, such as Stoddard dry cleaning solvent and silicone damping fluid, that cannot be reclaimed with the existing still. The new still will also be used to reclaim materials, such as paint thinners (e.g., MEK and toluene) and Coolanol 25R fluid, that were not being recovered because of inadequate capacity. The total potential savings in material costs and disposal costs for the new still is expected to be $315,000 per year.

7.1.3 Cost of Treatment

Cost data, developed for the three 3M batch distillation unit applications, the GCA batch distillation and fractionation process studies discussed above in Section 7.1.2, will be presented here followed by discussion of three recent studies not previously presented. The last three studies are a CH_2M Hill study of cost savings derived from a solvent recovery program at the Norfolk Naval Shipyard, a Pace Company examination of the costs of large scale recovery units[5], and a study by the U.S. Navy of the costs of small scale package batch distillation units.[15] Manufacturer profiles of the distillation units evaluation by the Navy are presented in Appendix B.

7.1.3.1 Cost Estimates for Small Packaged Batch Distillation Units--

The economic benefits to be derived from solvent recovery operations by the 3M Company in 1984 using small packaged batch distillation units has been described in Reference 12. For the three applications described earlier in Section 7.1.2, projected savings are as estimated in Table 7.1.10. As shown, cost savings based on test results, will be significant for the three applications.

TABLE 7.1.10. PROJECTED ECONOMIC BENEFITS

Application	Volume to be processed (drums /yr)[a]	Projected[b] savings ($/yr)	Estimated wet scrap processing operating cost ($/yr)	Net savings ($/yr)	Total estimated capital cost[c] ($)	Invest-ment payback period (month)
1. Separation of Low and High Boilers	96	23,000	1,400	21,600	7,000	4
2. Processing High Viscosity and High Solid Content Scrap	808	53,700	25,600	28,100	39,000	17
3. Processing Solvent Contaminated Industrial Refuse	1,800	137,000	31,300	105,700	53,000	6
4. Alternative to Utilizing Vendor Solvent Recovery Services	1,350	108,000	20,300	87,700	54,400	8

[a] 1 drum = 208 L

[b] The projected savings includes raw materials purchase cost reductions and reductions in waste transportation and disposal costs.

[c] The total estimated capital cost includes estimates for equipment, engineering, installation and contingency.

Source: Reference 12.

3M's evaluation also included a fourth application shown in the table, involving the processing of waste solvent currently shipped offsite to solvent recovery services. The plant generates 74,250 gallons of pumpable waste annually. The waste contains heptane, toulene, MEK, alcohol, and 1,1,1-trichloroethane with an average solids content of 10 percent. The utilization of in-house wet scrap processing technology would elminate the current reclaimer and transportation costs, the associated liability risk, and raw materials purchase cost. Payback period for an in-house system was estimated to be 8 months as shown in Table 7.1.10.

7.1.3.2 Cost Estimates for a Packaged Batch Distillation Unit--

GCA evaluated the performance of a Zerpa RX-35 recyclene unit used in combination with a DuPont Riston-SRS-120 still used to recover solvent wastes for a printed circuit board manufacturer.[13] Previously, the concentrated spent developer solution was sent offsite for disposal and raw material was then purchased for make-up. Use of the Zerpa RX-35 unit resulted in the recycling of 10,605 gallons of 1,1,1-trichloroethane (annual basis) which resulted in a payback period of 6 months. Projected net savings were $49,100/year, after deduction of operating costs of $8,300/year. This reclamation effort represents a significant reduction in waste volume (99+ percent), regulatory compliance costs, and possible future liabilities.

7.1.3.3 Cost Estimates for the Batch Fractionation Process--

As part of the Reference 13 study, for solvent recovery operations conducted at a printed circuit board manufacturing firm, GCA developed a cost analysis. A comparison was made between the cost of onsite recovery of Freon TF versus the costs of offsite recovery. Factors and cost estimates are presented in Tables 7.1.11 and 7.1.12 respectively. They are based on the quantities of waste solvent and still bottoms that were generated in 1984. Most of the cost factors (unit costs) in Table 7.1.11 are self-explanatory, however those pertaining to offsite residue disposal (or management) were generated by GCA survey and assumption. Based on discussion with several waste disposal firms, a per gallon cost was derived for the offsite recovery of spent solvent in the hypothetical case that onsite distillation was not practiced. In the former case, it was assumed that the waste mangement

TABLE 7.1.11. UNIT COSTS

Electricity	- $0.05/kw-hr
Steam	- $0.96/1,000 lb
Cooling water	- $0.25/1,000 gal
Operating Labor	- $15/hr
Engineering	- 10% of equipment cost
Other Capital Costs	- 10% of equipment cost
Annualized Capital	- Based on 10 years and 10% interest
Methyl Chloroform	- $4.50/gallon
Freon 113	- $11.92/gallon
Offsite Recovery of Spent Solvent (Residue Disposal)	- $0.25/gallon credit
Offsite Recovery of Still Bottom (Residue Disposal)	- No charge

Source: References 10, 13, 14, 15.

TABLE 7.1.12. ESTIMATED COST OF RECOVERY OF FREON/METHYL CHLOROFORM

Cost item	Onsite recovery		Offsite recovery	
	Quantity	Cost	Quantity	Cost
Capital Cost				
- Equipment	1	130,000	0	0
- Engineering	--	13,000	--	--
- Other	--	13,000	--	--
TOTAL CAPITAL		156,000		0
Annual O&M				
- Electricity	1.5 kw	600	--	--
- Steam	470 lbs/hr	3,800	--	--
- Cooling Water	4,302 gal/hr	9,100	--	--
- Labor	2,800 hrs/yr	42,000	--	--
- Maintenance	--	15,600	--	--
- Residue Disposal	119,500 gallon	0	295,800 gallon	(74,000)
TOTAL O&M		71,100		(74,000)
Annual Cost				
- Annualized Capitol	--	12,600	--	--
- Annual O&M	--	71,100	--	(74,000)
- Solvent Cost	23,900 gallon	190,900	176,300 gallon	1,408,000
TOTAL COST		274,600		1,334,000

Source: Reference 13.

facility would accept the still bottoms, containing 5-10 percent nonvolatiles, for no charge, but no credit. In the latter case, where the solvent would contain less than 1 percent nonvolatiles, the waste management facility would give the generating facility a 25 cent per gallon credit for each of the solvent types. Also, it was assumed that the industrial facility would pay two-thirds of the current price for virgin solvent.

The equipment cost is based on the use of a 1,200 gallon per day APV batch distillation system. The $130,000 FOB price includes a 28-foot distillation column with metal mesh packing, a 1,450 gallon batch pot, a U bundle reboiler, U bundle condenser, shell and tube vent condenser, bottom and top product pumps, bottom and top product shell and tube coolers, and instrumentation for automatic operation as provided by APV Crepaco (1986). The unit would be preassembled and include all valves and piping.

O&M costs for this system are based on operating this unit 24 hours per day, 350 days per year. This unit is operated virtually continuously as long as spent solvent is available for input. Since the unit is equipped with instrumentation to allow for automatic operation, it need not be monitored full time. Of 24 hours, 8 hours of operating labor was assumed to be required.

Onsite recovery of Freon results in a cost savings of approximately $1 million per year as compared to offsite recovery.

7.1.3.4 Study of the Norfolk Navy Shipyard Operation--

At the Norfolk NSY, approximately 15 gallons per day of numerous waste solvents including mineral spirits, ketones, and epoxy thinners containing paint pigments are generated in the paint shop during cleaning operations. Historically, the waste solvents have been disposed of at a cost of $7.80 per gallon. A nonfractionating batch still, Model LS-15V, manufactured by Finish Engineering (see Appendix B) was installed at Norfolk. This unit is equipped with a vacuum system which enables the still to recover solvents with boiling points of up to 500°F. Norfolk reported the cost of the unit to be $9,000 ($5,000 without the vacuum system). They reported recovering more than 50 percent of their waste solvents at a cost of about $0.05 per gallon.[14]

7.1.3.5 Cost Estimates For Moderate To Large-Scale Recovery Units--

In their 1983 report entitled, "Solvent Recovery in the United States, 1980-1990"[5], the Pace Company generated comprehensive cost data for a variety of solvent recovery technologies (base case flow rate of 200 gallons per hour). Costs were based on the threshold cost of recycled solvent; i.e., the costs required to provide various rates of return for installation and operation of a newly constructed recovery system. Costs for solvent recovery facilities located within an existing industrial plant were based on the following anticipated capital investment expenditures: process equipment (vessel, condenser, etc.), tankage, engineering, electrical, instrumentation and contingency. The majority of distillation systems assessed in the study are sold by vendors as modular packages including the vessels, an overhead condenser, decanter or receiver, and various pumps and motors. Tankage requirements will increase with the number of waste types to be processed and the processing volume. Pace assumed that cone bottom tanks would be purchased since they allow for greater ease of cleaning settled solids.

Engineering, electrical, and instrumentaion costs associated with designing and constructing a facility were assumed to be 20 percent of the process equipment costs. A contingency cost of 15 percent was included to cover any unanticipated costs. Capital costs are summarized in Table 7.1.13.

Operating costs include utility, maintenance (negligible), disposal and labor costs. Pace assumed that utilities such as steam could be easily obtained from existing units. Energy consumption costs for various solvents average 4 cents per gallon of recovered solvent at an electricity cost of 4 cents/kWh. It should be noted, however, that fractional distillation can be considerably more energy intensive with high reflux.

Disposal costs were proportional to throughput and increased with solids concentration in the feed. Pace assumed the bottoms product would be 45.5 percent solids and cost 54 cents per gallon for disposal. For most solvent wastes not already being recovered, such a high recovery may not be realistic. Depending upon expected recoveries relative to what is assumed by Pace, threshold costs will vary. Adjusted values can be derived by comparing the Pace estimated recovery to specific expected recoveries in addition to adjusting disposal costs. The Pace estimated disposal costs may be inaccurate

TABLE 7.1.13. CAPITAL COSTS FOR ONSITE SOLVENT RECOVERY SYSTEMS (1982 Dollars)

	Coil still			Scraped surface still					
Nominal Feedrate (gph)	50	100	200	7.5	25	50	100	200	300
Process Equiment	37,500	45,000	50,900	19,400	24,400	30,400	37,900	47,700	62,600
Tanks	18,500	18,500	37,000	18,500	18,500	18,500	18,500	37,000	37,000
Sub-Total (1)	56,000	63,500	87,900	37,900	42,900	48,900	56,400	84,700	99,600
Engineering, Electrical, Instrumentation (20% of (1))	11,200	12,700	17,600	7,600	8,600	9,800	11,300	16,900	19,900
Sub-Total (2)	67,200	76,200	105,500	45,500	51,500	58,700	67,700	101,600	119,500
Contingency 15% of (2)	10,100	11,400	15,800	6,800	7,700	8,800	10,200	15,300	17,900
Total	77,300	87,600	121,300	52,300	59,200	67,500	77,900	116,900	137,400

Source: The Pace Company. Reference 5.

depending upon the waste type or disposal method. Threshold costs may be lower for solvent waste used as a fuel or considerably higher for halogenated solvent residuals which must be incinerated.

Finally, labor requirements were assumed to be two employees per hour onstream at a cost of $14.42 per hour, including overhead. These labor requirements are high, especially for units which are often automated and operated with existing labor levels. The Pace base case was assumed to apply for the 200 gph flow rate with labor being proportional to the flow rate for the smaller units. Combined with the above assumptions for capital and operating costs and financial parameters, the threshold costs for onsite recovery are summarized in Table 7.1.14 for varying solids contents, 50 and 200 gph feed rates, and 15 and 30 percent net discounted cash flow (DCF).

TABLE 7.1.14. THRESHOLD COSTS[a] ($ PER GALLON) FOR ONSITE RECOVERY SYSTEMS FOR VARYING SOLIDS CONTENTS AND PERCENT NET DISCOUNTED CASH FLOWS (DCF)

Technology	Nominal flow rate (gph)	Percent DCF	Percent Solids			
			5	10	15	20
Coil Still	50	15	0.62	0.80	1.06	1.39
	200		0.40	0.53	0.71	0.97
	50	30	0.87	1.08	1.39	1.80
	200		0.49	0.64	0.84	1.13
Scraped Surface Still	50	15	0.66	0.76	1.01	1.33
	200		0.39	0.53	0.71	0.96
	50	30	0.80	1.00	1.30	1.69
	200		0.49	0.63	0.83	1.11

[a] Costs in 1982 dollars.

Source: Reference 5.

For most onsite facilities, threshold cost will be relatively insensitive to variations in equipment capital costs due to the effects of labor on overall recovered solvent cost. Pace concluded that a threshold change of only ±5 percent may result from capital cost fluctuations of 20 percent.

However, cost will be sensitive to changes in on-stream time (capacity factor). If the solvent recovery equipment were operated less than 40 hours per week, threshold costs could increase dramatically due to increased fixed cost per gallon recovered.

7.1.3.6 Cost Estimates for Small Packaged Stills--

The Naval Energy and Environmental Support Activity (NEESA) has assessed the costs of small to moderate sized batch stills and a larger continuous still, with results reported in Reference 15. The major cost parameters considered in evaluating the potential economics of a solvent reclamation program were as follows:

D - Cost of distillation unit ($)

E - Recovery efficiency of still (decimal fraction)

I - Cost of installation ($)

M - Cost of additional labor (varies with size and operational requirements of still; assume $0 for under 3,500 gallons per year, $2,500 between 3,500 and 13,000 gallons per year, and $7,500 for over 13,000 gallons per year)

S - Cost of solvent ($/gallon)

U - Cost of utilities in reclaiming solvent ($/gallon)

V - Volume of waste solvent generated by activity or shop (gallons)

W - Waste disposal costs for solvent and still bottoms ($/gallon)

(A/P:i:n) - Appropriate capital recovery factor to evaluate payback period.

These parameters may be combined to form an equation representing the parameter interactions at specific payback periods as follows:

$$V[ES+(1-E)W] - (A/P:i:n)(D+I) - UV - M = 0$$

Using this equation it is possible to calculate break-even volumes of solvents for various applications and payback periods. Minimum estimated quantities of solvent required to break even in 3 years (relative to land disposal), are as follows:

- Mineral Spirits: 1,500 gallons per year
- Degreasers: 500 gallons per year
- Waste Paint Thinner (Epoxy): 700 gallons per year

The following sections examine the economics of in-house solvent reclamation for the three major types of solvent.

Cold Cleaning Solvents--

The mineral spirits type solvents used for cold cleaning of metal parts tend to have relatively low cost, low volatility, and high boiling points. These factors make cost-effective recovery high volume dependent because of the more expensive reclamation equipment required and the low value of the solvent. Payback periods were calculated using the cost equation and the assumptions listed below.

Assumptions:

Cost of Still (D): $ 8,600 for under 3,500 gallons per year
$17,700 for under 3,500-13,000 gallons per year
$45,000 for 13,000-60,000 gallons per year

Installation Cost (I): 1.5 D

Recovery Efficiency (E): 0.95

Additional Manpower (M): See original assumptions

Solvent Cost (S): $1.75 per gallon

Utility Costs (U): $0.05 per gallon

Waste Disposal Costs (W): $1.00 per gallon, $2.00 per gallon, $3.00 per gallon

Discount Factor (i): 10%

Due to the high sensitivity to waste disposal costs for the small (15 gpd) and medium (55 gpd) size distillation units, economic analyses were conducted using three disposal costs. For the large distillation unit (250 gpd) where the waste disposal cost is less influential, the economic analysis was conducted at the median disposal cost of $2.00 per gallon. NEESA originally assumed a $0.25 per gallon utility cost. Case studies conducted by GCA and others report utility costs to be on the order of $0.05 per gallon. Working with the basis provided by NEESA, payback period curves were generated for the reduced utility costs in Figures 7.1.3 to 7.1.5.

Vapor Degreasing Solvents

Since solvents used for vapor degreasing are volatile and expensive, they are ideally suited for cost-effective reclamation. These low boiling solvents require the least expensive reclamation stills. Cost assumptions in developing Figure 7.1.6 are:

Cost of Still (D): $ 4,600 for under 3,500 gallons per year
$12,000 for 3,500 to 13,000 gallons per year
$30,500 for 13,000 to 60,000 gallons per year

Solvent Cost (S): $4.50 per gallon

Waste Disposal Cost (W): $2.00 per gallon

Other costs are the same as for cold cleaning solvents.

Paint Thinners--

The composition of waste paints and waste paint thinners varies markedly depending upon the manufacturer and application. Since the primary purpose of reclaiming paint thinners is for reuse in cleaning paint spray equipment, the exact composition is not important so long as the reclaimed solvent is compatible with the paint to be cleaned from the equipment. Since most paint thinners are mixtures, vacuum type distillation units are required since one or more components of the thinner usually have high boiling points. The assumptions used in developing the payback curves are those given for

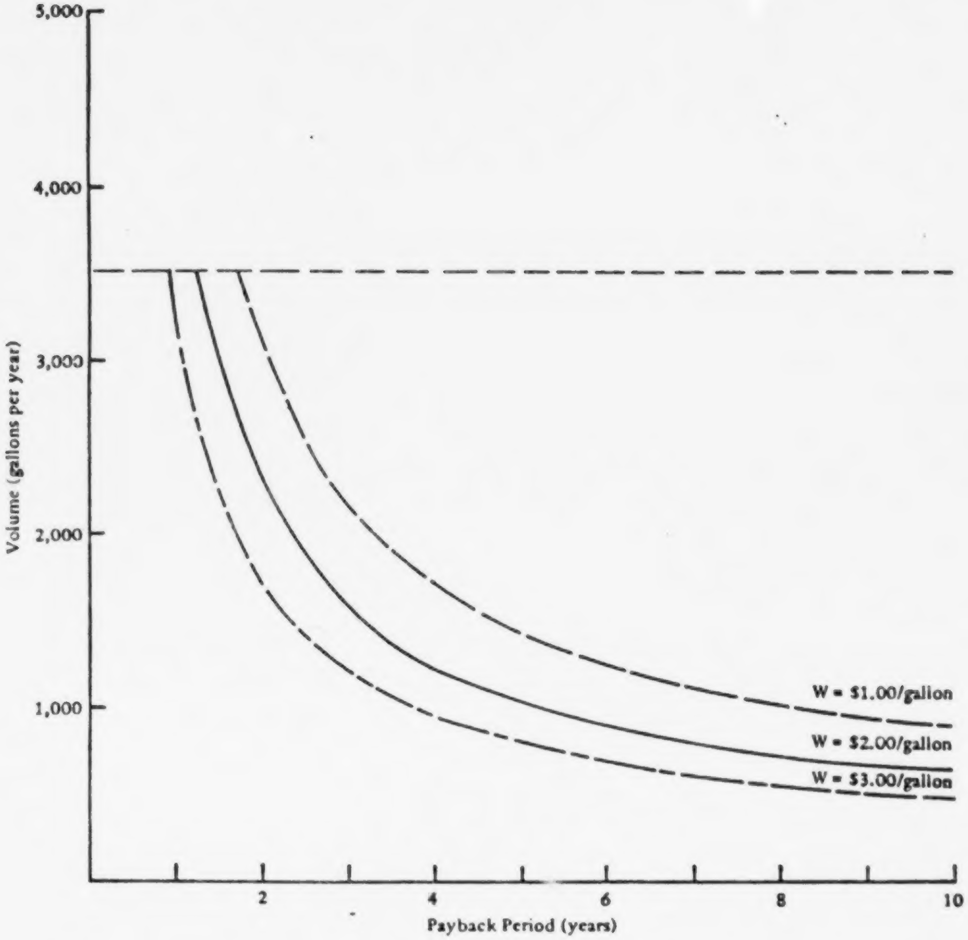


Figure 7.1.3. Reclamation of cold cleaning solvents via small batch stills (15 gpd).

Source: Reference 15.

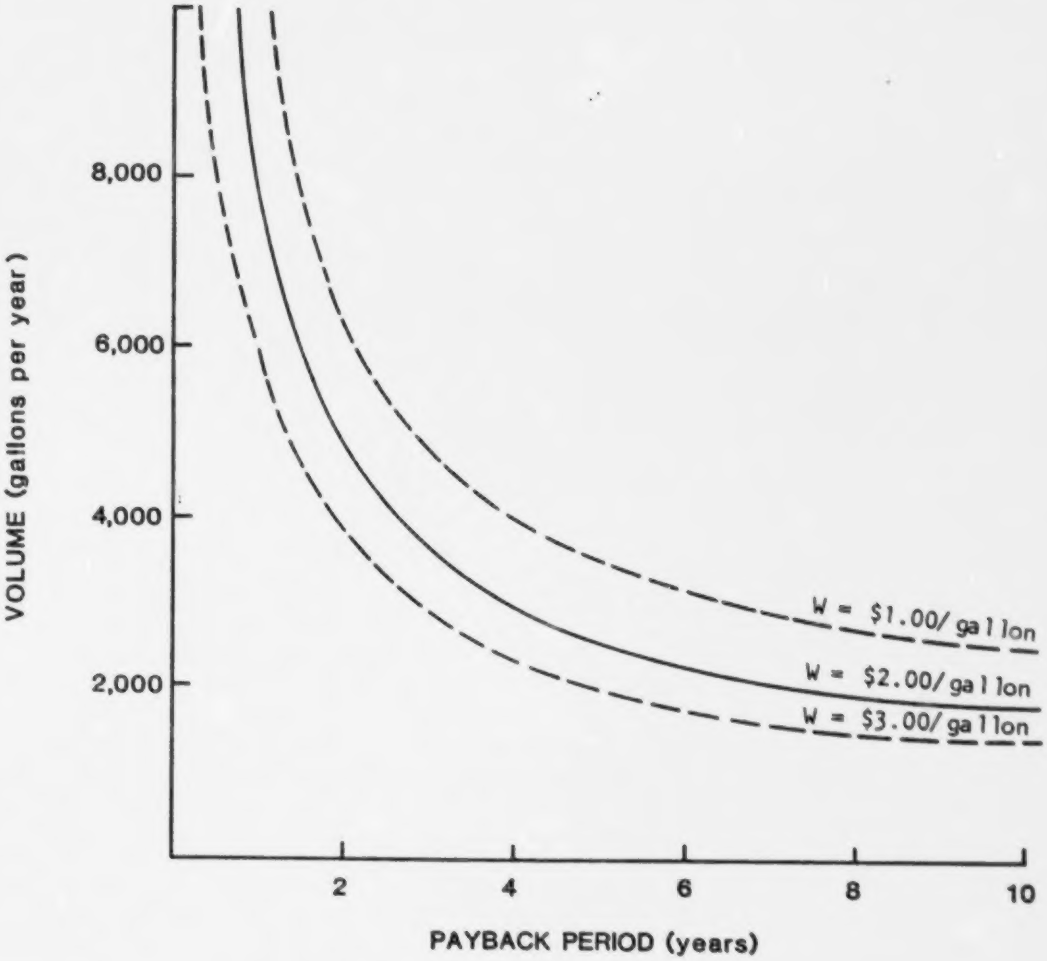


Figure 7.1.4. Reclamation of cold cleaning solvents via medium batch stills (55 gpd).

Source: Reference 15.

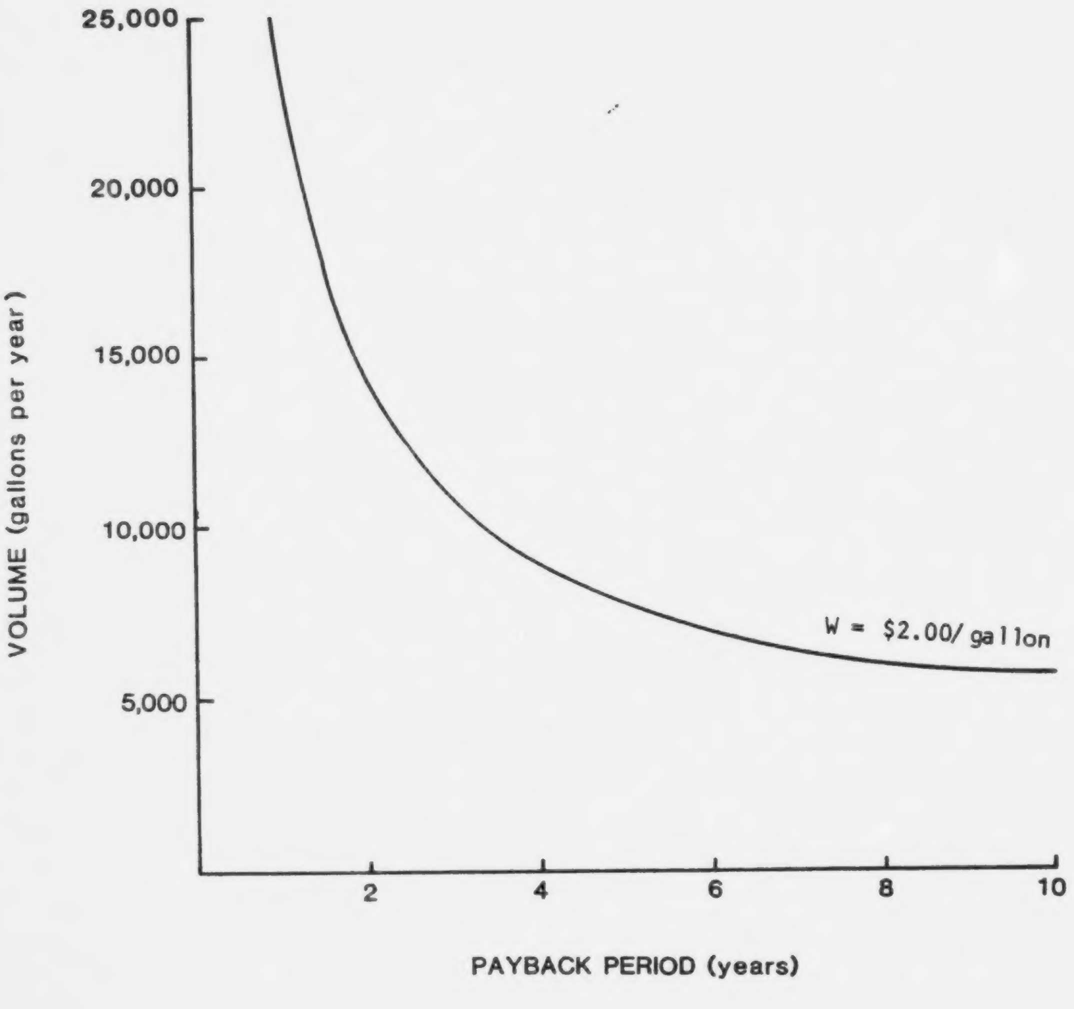


Figure 7.1.5. Reclamation of cold cleaning solvents via a large continuous still (250 gpd).

Source: Reference 15.

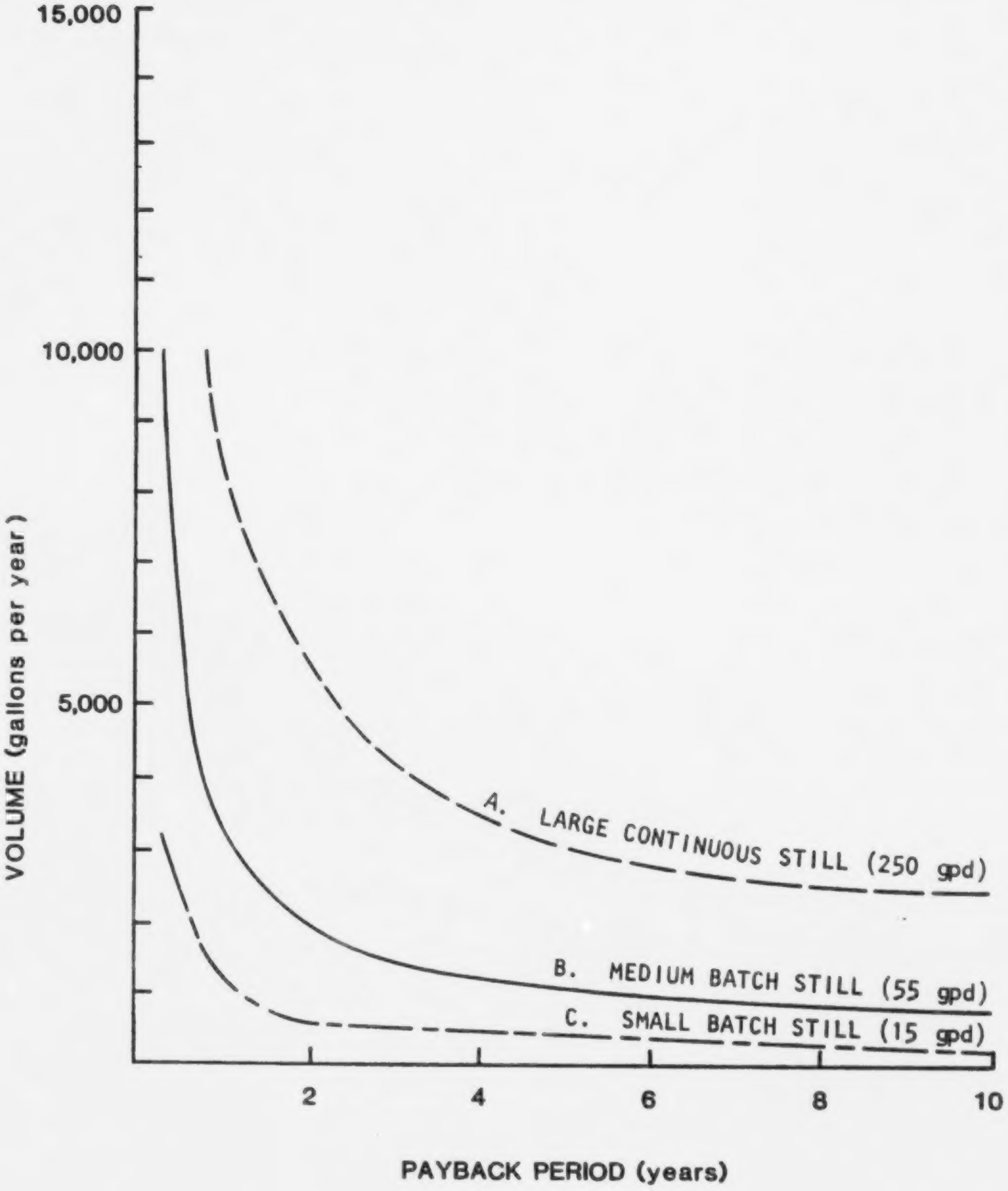


Figure 7.1.6. Reclamation of vapor degreasing solvents (chlorinated hydrocarbons, $4.50/gallon).

Source: Reference 15.

reclaiming cold cleaning solvents except that solvent costs range from $2.00 to $4.50 per gallon. Payback curves are given in Figures 7.1.7 and 7.1.8 for two solvent costs. Utility costs were not adjusted for these curves.

7.1.4 Overall Status

7.1.4.1 Availability/Application--

Distillation and fractionation are two of the most established unit operations. Many firms provide design services and manufacture equipment. The Chemical Engineers Equipment Buyers' Guide provides a comprehensive list of such firms. In December 1985, the Naval Energy and Environmental Support Activity (NEESA), presented the results of a package distillation equipment manufacturer's survey. The document provides detailed price, option (including safety features), and specification information for products from 17 different manufacturers of small batch and continuous units (< 60 gallons per hour). Table 7.1.15 lists some of the general specifications of the stills that were considered. Appendix B provides more detailed information including capital purchase cost information.

7.1.4.2 Environmental Impact--

The environmental impact of distillation processes for solvent recovery should be minimal. Apart from questions related to the disposal of still bottoms, other emissions, including air emissions from the condenser, do not appear to be significant.

7.1.4.3 Advantages and Limitations--

Distillation would appear to be a key technology for the recovery of solvent wastes. Based on well understood principles, its implementation is relatively straightforward and its economic benefits can be appreciable.

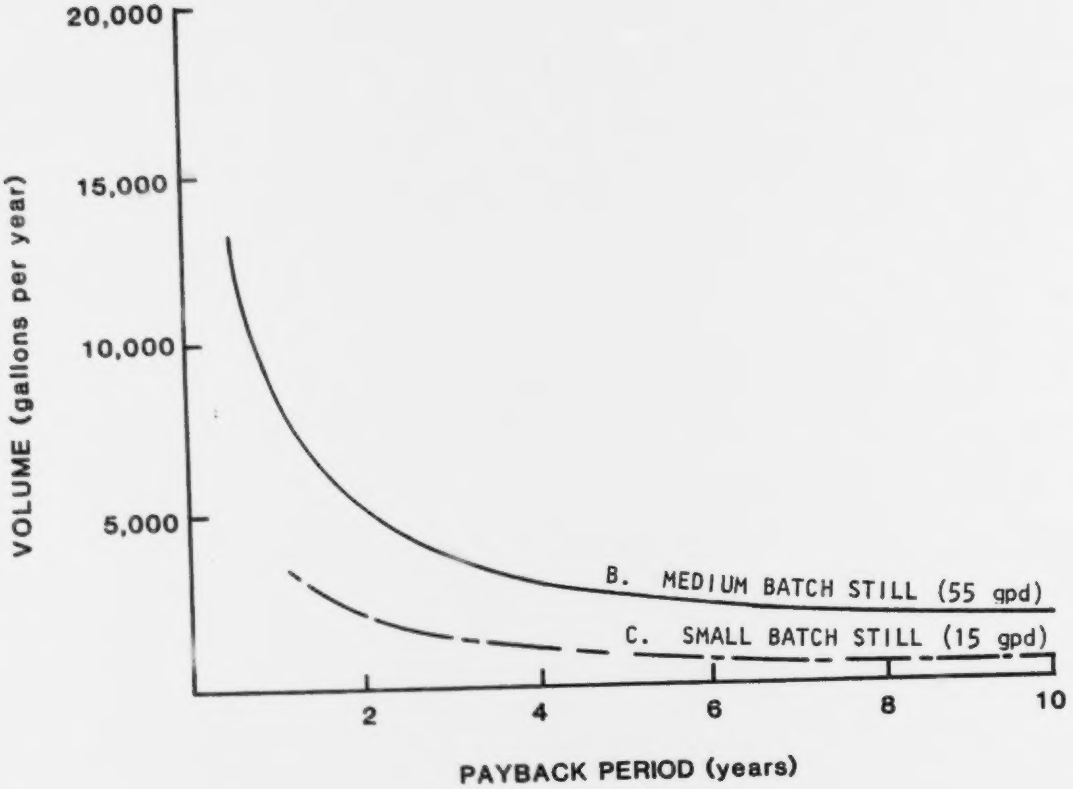


Figure 7.1.7. Reclamation of waste paint thinner ($2.00/gallon).

Source: Reference 15.

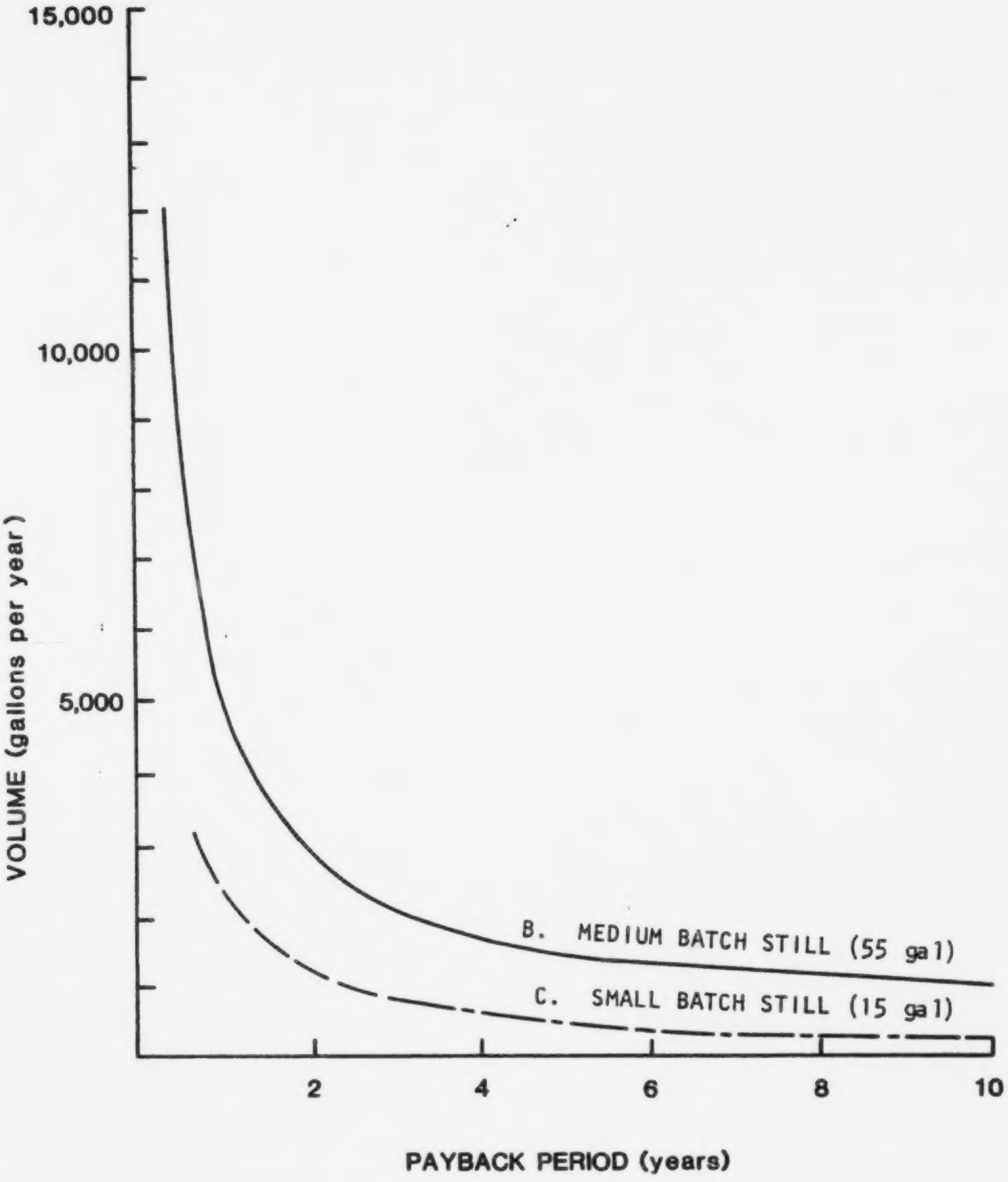


Figure 7.1.8. Reclamation of waste paint thinner ($4.50/gallon).

Source: Reference 15.

TABLE 7.1.15. COMMERCIALLY AVAILABLE SOLVENT STILLS[a]

Manufacturer	Solvent types	Maximum b.p.(F)	Explosion proof	Vacuum Available	Water Separator	Heating	Cooling
Alt. Resource Mgmt	All	500	X	X	X	Electric/Steam	Water
Baron-Blakeslee	Halogenated	350			X	Electric/Steam	Water/Refrig
Branson	Halogenated	350			X	Electric/Steam	Water/Refrig
Brighton	All	500	X	X	X	Hot Oil/Steam	Water
Cardinal	Halogenated	350	X			Electric	Refrig
DCI	All	500	X	X	X	Dir.Stream Inj.	Water
Disti	All	500	X	X	X	Hot Oil/Steam	Water
Finish Engineering	All	500	X	X		Electric/Steam	Water
Hoyt		All	350	X		Hot Oil	Water
Lenape	Halogenated	350			X	Electric	Water/Refrig
Phillips	Halogenated	350			X	Electric/Steam/Gas	Water
Progressive Recovery	All	500	X	X		Hot Oil/Steam	Water
Ramco	Halogenated	350				Electric/Steam	Water/Air
Recyclene	All	420	X			Hot Oil	Water
Unique Industries	Halogenated	350			X	Electric/Steam/Gas	Water/Refrig
Venus	All	210	X			Electric	Water/Refrig
Westinghouse	Halogenated	350			X	Electric	Water/Refrig

Source: Reference 4.

[a] Capacity less than 60 gallons per hour.

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7.2 EVAPORATION PROCESSES

Available evaporation equipment designs include simple stills, flash evaporators, forced circulation evaporators, and falling film and agitated thin film evaporators. All designs are capable of concentrating nonvolatile components of waste mixtures. However, in cases where fouling, foaming, high viscosity, thermal degradation or other factors present potential operational problems, agitated thin film evaporators provide the most versatile service.[1] They also represent the most effective, high volume evaporation equipment which is capable of reducing viscous wastes to low residual organics.[2] This is a direct result of high mass transfer rates achieved through turbulence. For these reasons, a majority of large commercial solvent recycling companies use agitated thin film evaporators (ATFEs) as indicated by several industry surveys.

The emphasis in this section will be on the agitated thin film designs because of their widespread use and applicability in reclaiming solvent wastes which are too viscous or otherwise too difficult to recover in conventional distillation equipment. Extensive reference to conventional equipment was provided in Section 7.1.

7.2.1 Process Description

Liquid waste is fed to the top of ATFEs where longitudinal blades mounted on a motor driven rotor centrifugally force the waste against the heat transfer surface; i.e., the inside wall of the cylindrical vessel. This surface is enclosed in a heating jacket which usually employs steam or hot oil as the heating medium (temperatures up to 650°F).

The agitation and liquid film are maintained by the blades as they move along the heat transfer surface. The blade tips typically travel at 30 to 40 feet per second at clearances of 0.007 to 0.10 inches which creates high turbulence (see Figure 7.2.1). This facilitates efficient heat and mass transfer, shortens required waste residence time and creates a degree of mixing which maintains solids or heavy molecular weight solutes in a manageable suspension without fouling the heat transfer surface. Mass diffusivities in ATFEs can be increased by 1,000 to 10,000 times over

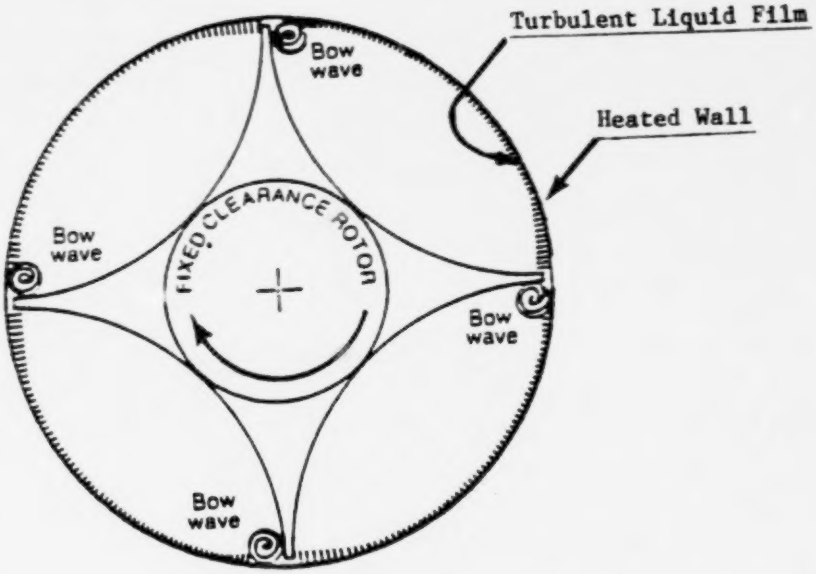


Figure 7.2.1. Cross section of agitated thin film evaporator.

Source: The LUWA Corporation
Bulletin EV-24, 1982.
Reference 3.

nonagitated designs.[2] To further promote separation, the unit is usually operated under vacuum conditions which permits lower temperature processing of thermally unstable mixtures.

Ultimate recovery in all evaporation/distillation units is limited by vapor-liquid equilibrium constraints as discussed in detail below. However, for viscous wastes, economical recovery is further limited by waste viscosity as a result of decreasing diffusivity of volatile compounds through the waste as viscosity increases. As diffusivity decreases, resistance to overall mass transfers into the gas phase increases. However, this effect is less pronounced in ATFEs relative to other evaporator designs due to high turbulence and large exposed waste surface area.

Finally, thermodynamic properties of the waste and ATFE operating pressure set a limit on ultimate recovery imposed by vapor-liquid equilibrium constraints. Material will boil when its vapor pressure reaches the operating pressure of the ATFE. Waste vapor pressure for miscible fluids is equal to the sum of the partial pressure of each volatile species. Partial pressure of each component is, in turn, equal to its molar concentration multiplied by the pure component vapor pressure and a constant which is dependent on the ideality of the solution. Thus, operating pressure and partial pressure determine the minimum attainable (i.e., equilibrium) concentration of each volatile species in solution. High separation efficiency will be associated with low system pressure, high pure component vapor pressure, high activity coefficient, high Henry's Law constant, and low solubility (decreases with temperature). Theoretically, very high separations can be achieved for highly volatile compounds in systems of low liquid phase miscibility. Ultimate recovery will depend on the extent to which equilibrium is achieved which will be limited by diffusive resistance to mass transfer and residence time in the system.

Residual solvent concentrations below 1,000 ppm have been routinely achieved and a concentration below 100 ppm can be achieved if conditions are optimal. Except in unusual circumstances (e.g., immiscible fluids), the sole use of ATFE cannot be expected to yield residual solvent concentrations in the low ppm range.

7.2.1.1 Pretreatment and Post-Treatment Requirements--

A schematic of an ATFE and associated pretreatment and post-treatment options is shown in Figure 7.2.2. As shown, the pretreatment techniques most commonly applied to wastes undergoing ATFE are a previous solvent recovery process, oil or suspended solids removal or a dissolved solids concentration process. The most cost-effective application of a ATFE is in treating viscous wastes which are generally not amenable to treatment using other, less expensive evaporative processes. In many cases, the source of these wastes will be bottoms products from conventional evaporation/distillation processes. These processes have been described previously (Section 7.1).

Constraints on the acceptable viscosities of wastes differ between manufacturers and specific unit types. In general, specially designed ATFEs can process wastes with viscosities up to 1,000,000 cps as indicated in Table 7.2.1 and Figure 7.2.3 which presents equipment selection guides for evaporator products based on waste viscosity.[1,4]

Post-treatment methods are also identified in Figure 7.2.2. These basically include further refinement of the overhead product, through water removal or separation of solvent mixtures, and further solvent recovery or disposal of bottom products.

The recovered solvent may be used as is or further purified through decanting, dehydration or fractionation. In cases where the waste feed is a mixture of solvents, separation by fractional distillation is sometimes justified by the increased value of the separated components.

Further recovery of bottoms from ATFE treatment of organic wastes is generally not considered practically achievable in liquid handling equipment. However, in some cases a drum dryer, centrifuge or other solids handling equipment might be employed depending on the nature of the waste. The residue is often solidified and landfilled, incinerated, or burned as fuel if the Btu value, chlorine content, ash content and viscosity are within required specifications.

Further treatment of aqueous ATFE bottoms will generally be required to remove remaining volatiles and other contaminants. Candidate technologies include steam and air stripping, carbon adsorption, or biological treatment if toxic contaminant concentrations are low.

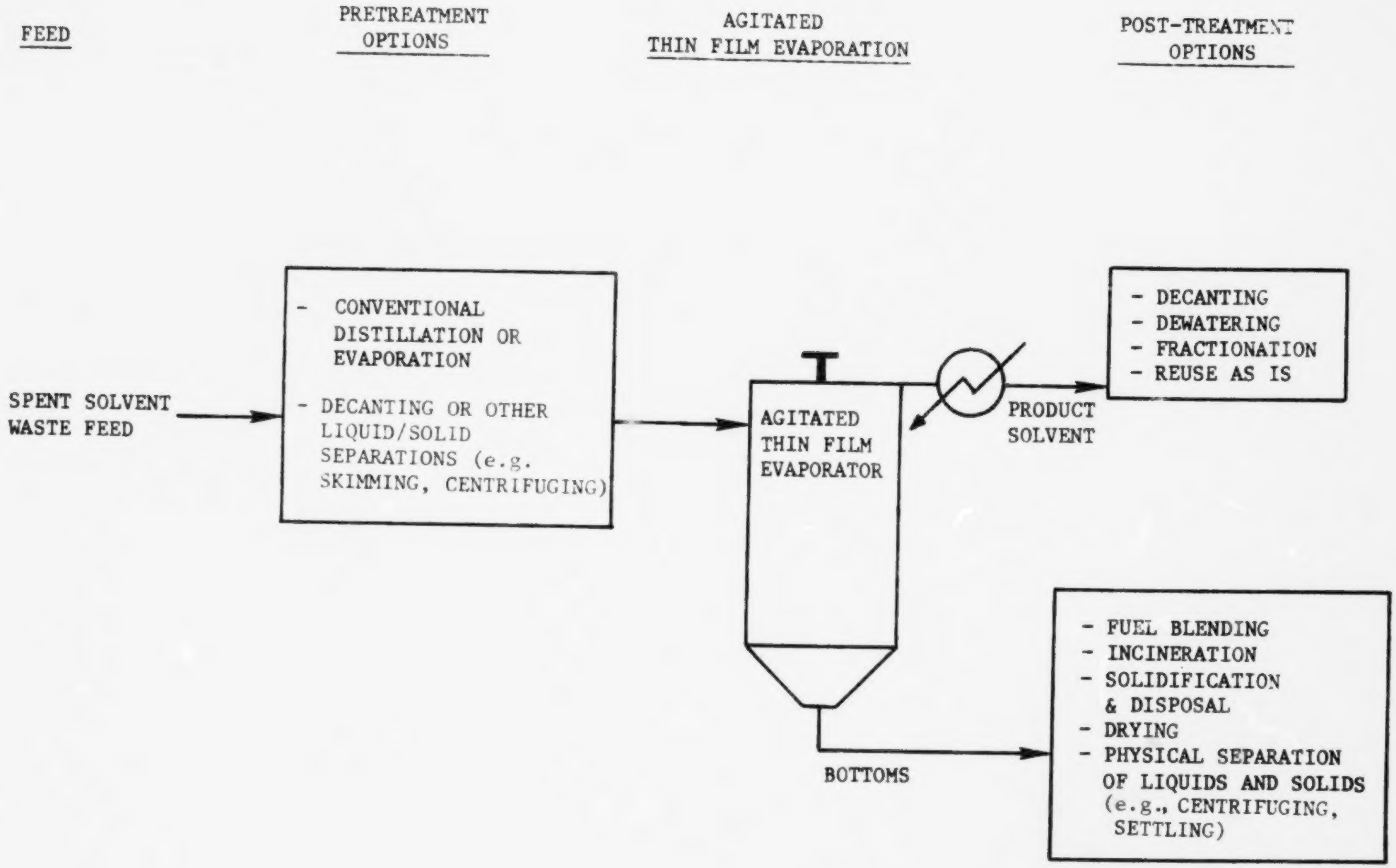

FEED
PRETREATMENT OPTIONS
AGITATED THIN FILM EVAPORATION
POST-TREATMENT OPTIONS
SPENT SOLVENT WASTE FEED
- CONVENTIONAL DISTILLATION OR EVAPORATION
- DECANTING OR OTHER LIQUID/SOLID SEPARATIONS (e.g. SKIMMING, CENTRIFUGING)
AGITATED THIN FILM EVAPORATOR
PRODUCT SOLVENT
- DECANTING
- DEWATERING
- FRACTIONATION
- REUSE AS IS
BOTTOMS
- FUEL BLENDING
- INCINERATION
- SOLIDIFICATION & DISPOSAL
- DRYING
- PHYSICAL SEPARATION OF LIQUIDS AND SOLIDS (e.g., CENTRIFUGING, SETTLING)

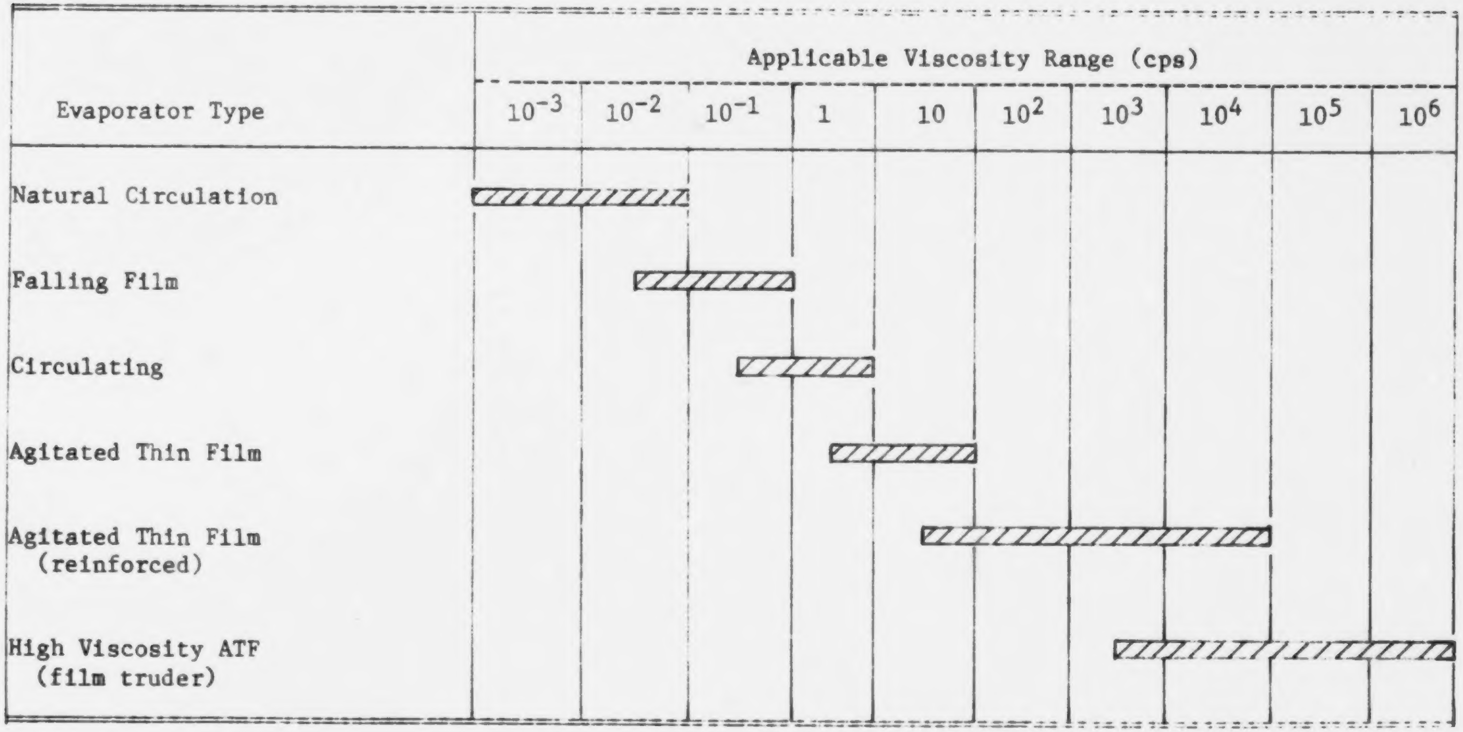
Figure 7.2.2. Treatment train using an agitated thin film evaporator.

TABLE 7.2.1. KEYS TO SELECTING KONTRO THIN FILM EVAPORATORS

		Horizontal Agitated Thin Film Evaporator	Vertical Agitated Thin Film Evaporator	High Viscosity ATFE (Film Truder)	Conventional Evaporator
Liquid Property	Low viscosity 10,000 cps or less	++	++	-	-
	Medium viscosity up to 50,000 cps	++	+	-	X
	High viscosity up to 1,000,000 cps	X	X	++	X
	Slurry	+	+	-	X
High vacuum evaporation		++	++	++	++
High concentration		++	-	-	-
Residence time control		++	+	-	X

Note: ++ = Particularly suitable
+ = Suitable
- = Usable in special cases
X = Unusable

Source: Reference 4.



Source: Reference 1.

Figure 7.2.3. Selection of Luwa Evaporators based on waste viscosity.

7.2.1.2 Operating Parameters and Design Criteria--

ATFEs are suited to treatment of concentrated, nonvolatile organic wastes contaminated with water, and aqueous wastes with volatile organic concentrations above 5 percent which are not amenable to treatment using less expensive conventional evaporation/distillation technologies. Typically, waste viscosity (feed or bottoms) is the restrictive waste characteristic which results in adoption of ATFE as the preferred technology. Consequently, pretreatment requirements are less stringent and may be reduced to gross solid removal or waste concentration through decanting.

Design and operation of an evaporator depends on the waste characteristics and desired recovery efficiency. Ultimate recovery may be restricted due to limiting waste characteristics or deliberately restricted based on the competing economics of processing, residual post-treatment and raw solvent purchase costs. Recovery will be a function of operating temperature, pressure, heat transfer and residence time. For recovery to low residual organics, particularly in viscous wastes, mass transfer resistance presents the biggest obstacle to recovery efficiency.[2]

Operating system temperature and pressure are limited by waste type and equipment design. Temperature must be higher (0 to 30°F) than the boiling point of the material, which is to be recovered as the overhead product, and sufficiently high to maintain a minimum waste viscosity. Maximum temperature (less than 650°F) may be limited by explosion limits or by the decomposition temperature of the recoverable materials, which is of particular concern for some halogenated organics (Section 7.1). Operation at low pressure reduces the temperature required to reach the boiling point. It also enables higher recovery rates to be achieved, as discussed previously. The lower limit of pressure is restricted by cost and equipment design. Typical system pressures range from atmospheric to 2 mm Hg.

For a given flow and desired recovery, an ATFE system has to be designed to produce a specific evaporation rate. Evaporation rate depends on temperature and pressure as discussed above, heat transfer surface area, waste type and heat transfer coefficient. Figure 7.2.4 and 7.2.5 show the relationship between heat transfer surface area, waste type and evaporation rate for a Cherry-Burrell ATFE (Turba-film processor).[5] Figure 7.2.6 shows the same relationship, based on unit area of heat transfer surface, for a LUWA ATFE.[3] As shown, high heat transfer surface area is required to evaporate

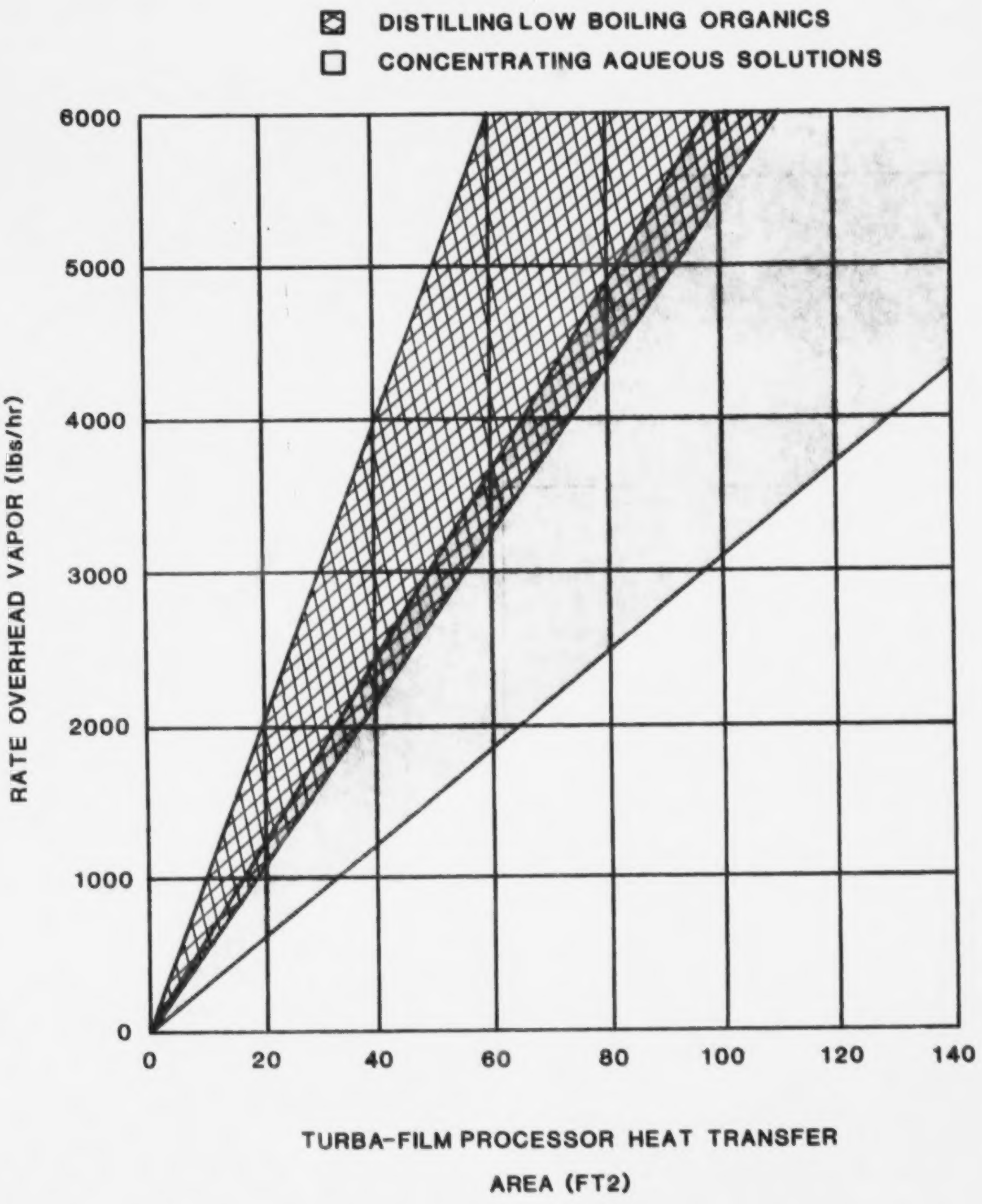


Figure 7.2.4. Required heat transfer surface area for distilling low boiling organics and concentrating aqueous solutions*.

*Source: Cherry-Burrell, Reference 5.

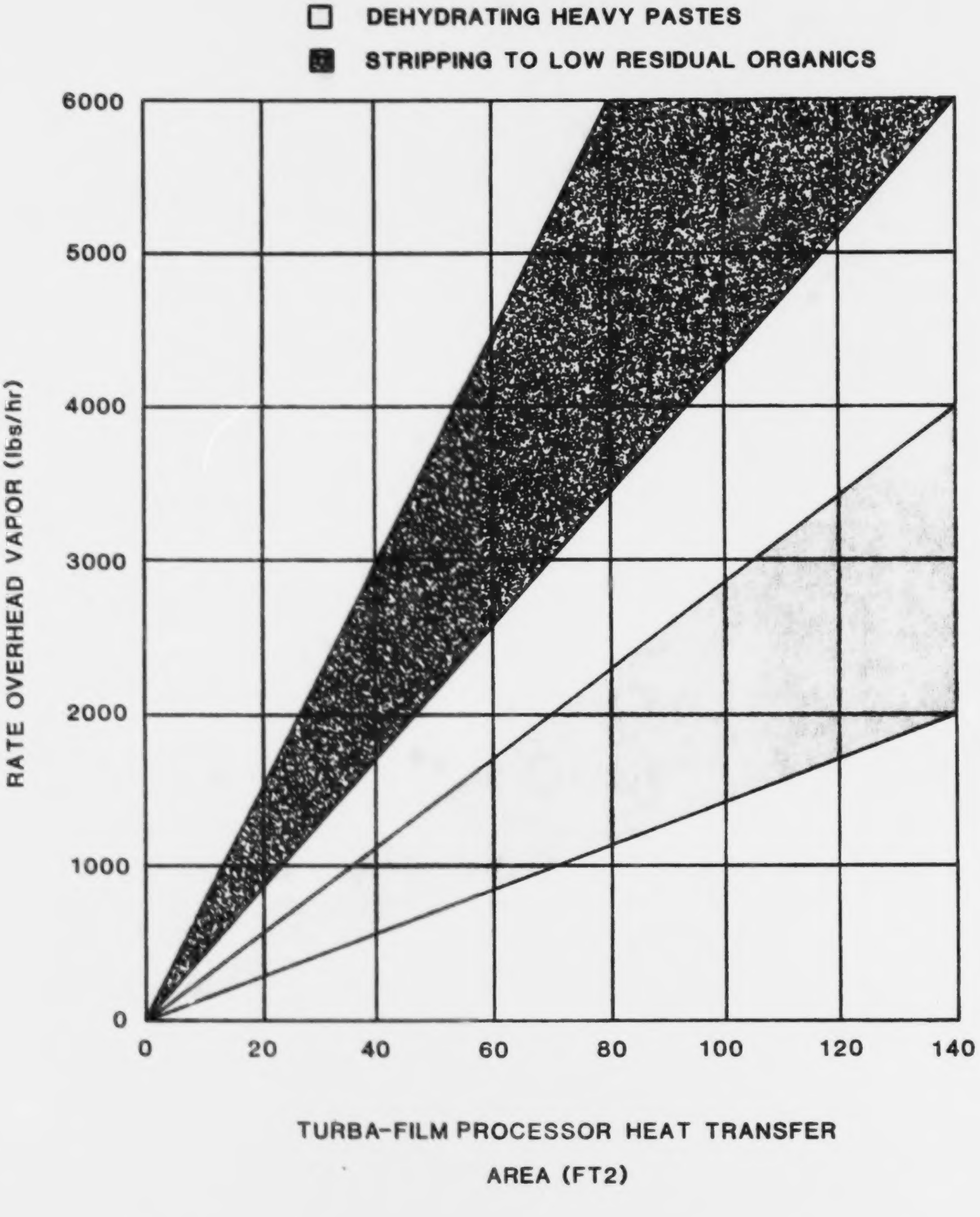
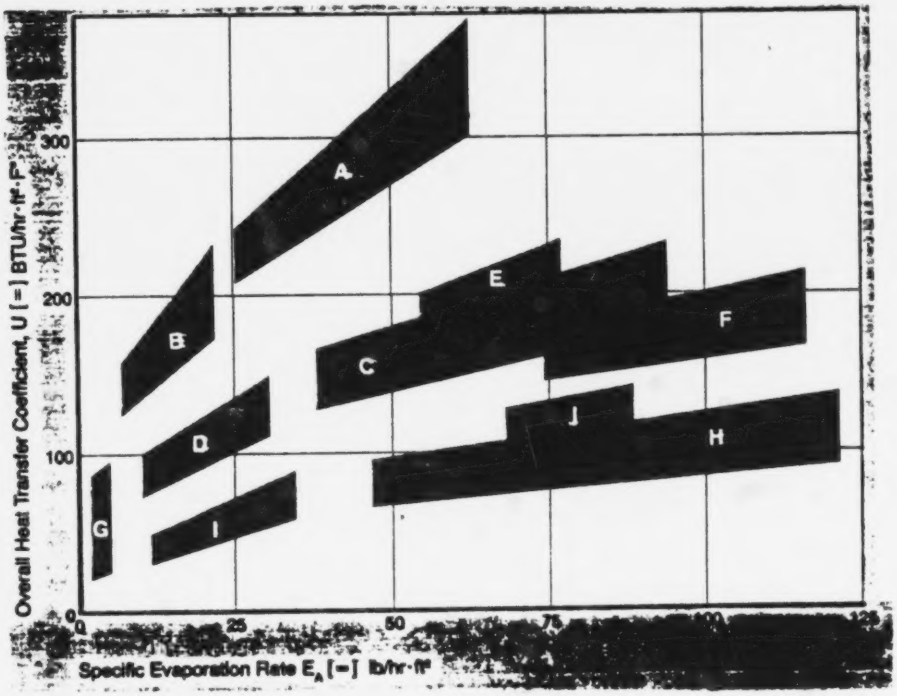


Figure 7.2.5. Required heat transfer surface area for dehydrating heavy pastes and stripping wastes to low residual organics*.

*Source: Cherry-Burrell, Reference 5.



Heating Medium: dry and saturated steam

A	Concentration of aqueous solutions
B	Dehydration of organics
C	Distillation of organics
D	Stripping of low boilers from organics
E	Reboiler service
F	Solvent reclaiming
G	Deodorization

Heating Medium: Dowtherm or hot oil

H	Distillation of high-boiling organics
I	Stripping of high boilers
J	Reboiler service

Figure 7.2.6. **Heat transfer and evaporation rates in Luwa Thin Film Evaporators.**

solvents from aqueous wastes and highly viscous materials; e.g. waxes and pastes. Aqueous wastes, because of their low viscosity, are often handled in conventional evaporation equipment.

In summary, increased evaporation rate can be attained by increasing heat transfer surface area, operating at the high temperature limit, or operating at the low pressure limit. However, if low concentration of VOCs in the bottoms product is desired, mass transfer limitations will shift optimal design toward high transfer area, increased turbulence and increased residence time.

Typical ATFE system operating data are summarized in Table 7.2.2.[6] As shown, heat transfer surface area, steam consumption and cooling water requirement vary directly with solvent recovery rate. However, electricity requirement drops per unit of solvent quantity recovered thus providing a slight drop in unit operating costs as capacity increases. Throughput of ATFEs is generally high. If waste solvents are generated in low quantities, package distillation units capable of handling high solids wastes may be more economical (see Section 7.1).

Commercially available evaporator equipment design parameters are summarized as follows.[2] Evaporators range from 1 to over 400 square feet of heat transfer surface with liquid throughput ranging as high as 250 lb/hr/ft^2. Overhead to bottoms splits for lightly contaminated fluids can be as high as 100 to 1 with controlled residence times of up to 100 seconds. Blade tip speeds of nonscraping designs average 30 to 40 ft/sec while scraping blades average 5 to 10 ft/sec. Some units come equipped with variable clearance while scraping blades are typically spring mounted or maintain contact with the wall as a result of centrifugal force. Operating temperatures range up to 650°F and pressure ranges from 2 mm Hg to atmospheric. Finally, configurations of commercially available equipment include vertical or horizontal shells, cylindrical or tapered design and cocurrent, countercurrent or separated vapor/liquid flow.

7.2.2 Demonstrated Performance

Actual performance data from commercially operated units, conducted in accordance with EPA Quality Assurance/Quality Control requirements, are limited to EPA sponsored studies as reported by GCA (1986)[7] and the Research solvents from aqueous wastes and highly viscous materials; e.g. waxes and pastes. Aqueous wastes, because of their low viscosity, are often handled in conventional evaporation equipment.

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TABLE 7.2.2. TYPICAL AGITATED THIN FILM EVAPORATOR DESIGN CHARACTERISTICS

Solvent Recovery (gal/hr)	Heat Transfer Surface Area (ft^2)	Utilities[a]			System Dimensions L x W x H, (ft)
		Heating Btu/hr (1000)	Cooling Water (gpm)	Electricity (KW)	
40	4.2	79	5	1.5	4 x 6 x 10
85	8.8	168	11	1.5	4 x 6 x 11.5
130	13.4	251	16	3.5	4 x 6 x 13
240	25	474	30	3.5	5 x 8 x 11.5
500	51.2	989	63	4	5 x 8 x 14

[a] Based on an average latent heat of vaporization of 175 Btu/lb and preheating feed by 200°F.

Source: Reference 6.

Triangle Institute (1984).[2] Other data generated by GCA and Metcalf & Eddy under studies currently being performed for the U.S. EPA were not available at the time this document was prepared.

As part of GCA and RTI's studies, a cost assessment was made for each of the four ATFEs which were sampled. None of the units studied demonstrated a capability of reducing volatile concentration in the bottoms product to low ppm levels. The following discussion summarizes the performance data for these units.

7.2.2.1 Thin Film Evaporator and Milsolvrator[7]--

GCA performed an evaluation of an ATFE in 1986 as part of an EPA sponsored study to obtain background information on alternative technologies to support the RCRA land disposal ban. An oil heated, batch LUWA ATFE was evaluated at Milsolv Corporation along with a still bottoms processing unit called a Milsolvrator. The latter consisted of large, jacket heated, inclined cylinder equipped with an internal auger to convey solids. The equipment operating and design features and test results are summarized below.

The LUWA ATFE contains an internal stainless steel rotary blade which spins at approximately 385 rpm with a 0.20 mm clearance between the blade tip and internal evaporator wall. The heat transfer surface area is 43 square feet and is heated by a hot oil jacket. The unit is operated under vacuum to enhance recovery, and is equipped with an optional recycle loop to recirculate bottoms if required. Process data during the three test runs are summarized in Table 7.2.3.

Milsolv operates the unit to achieve as high a reclaimed solvent yield as possible when processing halogenated solvents. However, a small percentage of nonhalogenated solvents are allowed to remain in the bottoms to ease handling and improve the fuel value. All bottoms are shipped offsite to a fuel blending facility or are shipped directly to a cement kiln for use as a supplemental fuel at an average disposal cost of $0.26 per gallon.

Three days of sampling were performed on the ATFE during which time one halogenated waste (F001) and two nonhalogenated wastes (F003 and F005) were processed. Table 7.2.4 summarizes the principal organic components of the waste streams. As shown, the halogenated waste was recovered to the greatest extent. However, the ATFE was only able to reduce the bottoms concentration

TABLE 7.2.3. PROCESS DATA FOR LUWA THIN FILM EVAPORATOR RUNS

Run Number	1	2	3
Date of Test	12/4/85	12/3/85	12/5/85
Total Gallons Processed	340	2835	3910
Time to Process Batch (hours)	4.25	20.6	17.0
Average Feed Rate (gal/min)	1.3	2.3	3.8
% Yield as Distillate	69.8	37.6	45.8
Average Temperature: Hot Oil Jacket in to the LUWA (°F)	311	318	327
Average Temperature: Hot Oil Jacket exiting the LUWA (°F)	304	307	317
Average Coolant Temperature (°F)	49	49	51
Average Distillate Temperature (°F)	48	45	52
Average Vacuum Surge Tank Temperature (°F)	52	51	52
Average Vacuum (in Hg)	5.6	7.1	25.5

Source: Reference 7.

TABLE 7.2.4. PERCENT BY WEIGHT OF PRINCIPAL ORGANIC COMPONENTS

Run 1

	Waste Quantity (gal)	Trichloroethylene	Solids
Waste Feed	342	98.14[a]	1.86
Distillate	239	99.9[a]	0.008
Still Bottoms	103	74.7	15.2

Run 2

	Waste Quantity (gal)	Ethanol	n-propanol	Ethyl acetate	n-propyl acetate	Solids
Waste Feed	2,835	24	7.7	24	9.8	11.8
Distillate	1,066	30	4.9	39	10	0.035
Still Bottoms	1,769	20	14	8.3	11	36.5

Run 3

	Waste Quantity (gal)	2-Butanone	Toluene/Heptane	Solids
Waste Feed	3,910	1.7	51	7.44
Distillate	1,791	1	46	0.033
Still Bottoms	2,119	2.8	54	23.7

[a] Based on solids content. GC analysis and density measurement yielded greater than 100% trichloroethylene based on an average of 3 samples.

Source: Reference 7.

of trichloroethylene to 75 percent with a waste volume reduction of 70 percent. The nonhalogenated wastes experienced a volume reduction of only 42 percent with 55 percent solvent remaining in the waste. Operational difficulties during the first run required solvent feed rates at approximately one-third of design level which may have had a negative impact on recovery rate.

GCA also collected samples from the processing of solvent contaminated waste in the Milsolvrator. However, these data were not yet available at the time this document was prepared. The Milsolvrator represents a unique design in high solids processing equipment although company officials still consider it to be in the design stage. Since units like these are likely to become more widely applied treatment methods in response to the land disposal ban, a description of the unit is provided below.

Waste is fed to the Milsolvrator manually, whereby an operator scoops the waste from a drum and places it in a grinder. Shredded waste is introduced into the elevated end of a long (20 ft) horizontal cylinder. A screw auger transports the waste through the cylinder. The clearance between the screw auger and the outside wall is an eighth of an inch. The cylinder is heated by a hot oil jacket which is capable of achieving an internal temperature of 550°F. The unit operates under 15 in. Hg vacuum. As the waste is heated during its path down the cylinder, solvent vapors are released, collected by a manifold system, then passed through a mist entrainer and condenser and collected in a receiving tank.

The solids portion of the waste traverses the entire length of the cylinder and is discharged to a receiving drum. This drum is attached directly to the Milsolvrator with a rubber o-ring seal in order to maintain the unit under vacuum. The residual solids discharged from the unit have passed EP-Toxicity tests.

7.2.2.2 Thin Film Evaporator - Plant A[2]--

The LUWA thin film evaporator at Plant A processes organic wastes, including sludges, from the furniture, chemical, dry cleaning and paint industries. The sludges include dirt and grease, paint films, particulates and insoluble organic materials. Since the still bottoms are used as a fuel substitute, the ATFE is operated to maintain pumpable bottoms containing less than 1 percent chlorides and an energy content greater than 28,000 kJ/L

(100,000 Btu/gal). Distillation bottoms are shipped offsite and utilized as fuel in cement and expanded aggregate kilns. Process economics require that 60 percent or more of the waste be recoverable. On average, 70 to 95 percent of the material is stripped off as overhead product which may be further refined in a fractionation column depending on the product's intended end use.[2]

The LUWA Thin Film Evaporator System at Plant A consists of a 4.0 m^2 (43 ft^2) heat transfer surface area LUWA Evaporator complete with an entrainment separator, condenser, feed pump, bottoms pump, distillation pump, vacuum system, and instrumentation. Evaporator feed rate and system pressure (vacuum) are determined based on the material being processed. A typical feed rate is 23 L/min (6 gpm), but may range from 4 to 45 L/min (1 to 12 gpm). Steam, controlled at about 30°C (54°F) above the boiling point of the distillate, is typically used as the heating medium. The cooling water for the overhead condenser is generally maintained in the range of 10 to 16°C (50 to 60°F), with a flow rate of about 1,500 L/min (400 gpm).

RTI reports that the thin film evaporator at Plant A can be used in the following applications:

1. Removal of VOCs from organic streams which may contain viscous high molecular weight organics or solids.
2. Removal of VOCs from sludge such as insoluble organics and particulate solids.
3. Concentration of aqueous sludges such as insoluble organics and particulate solids.
4. Removal of VOCs from aqueous streams where the VOC volatility is higher that that of water.
5. Removal of water from streams containing relatively high concentrations of organics of lower volatility than water (water removed as overhead product).

During RTI's field visit to Plant A, a waste consisting of mixed xylenes with a small amount of solids and approximately 5 percent VOCs was being processed through the thin film evaporator. The VOCs included several solvents of concern as listed in Table 7.2.5. Since this material contained few solids, approximately 95 percent of the feed was being taken overhead, leaving bottoms which were acceptable for fuel.

The data obtained from samples of the feed, bottoms, and the overhead product (shortly after process startup) are presented in Table 7.2.5. Removal efficiency estimates in excess of 99 percent were reported for the three chlorinated solvents, based on headspace analysis and the overall recovery rate of 95 percent. Toluene removal efficiency was reported as 95.4 percent. Further details of the estimation procedure used were not available. Recovery rates would be less than these values since appreciable, but unknown, quantities of these solvents were reportedly lost through the vacuum pump vent.

7.2.2.3 Thin Film Evaporator - Plant B[2]--

Plant B reclaims contaminated solvents and other chemicals through evaporation and distillation. About 10 percent of the incoming chemicals are contaminated products with the remainder being classified as hazardous waste. Approximately 85 percent of the reclaimed chemicals are returned to the generator with the remainder marketed to other suitable end users.

Processing equipment include two Votator ATFEs, two distillation reboilers, eight fractionation columns, one caustic drying tower, support facilities and waste transport and storage equipment. Plant B processes wastes from the chemical, paint, ink, recording tape, adhesive film, automotive, airlines, shipping, electronic, iron and steel, fiberglass and pharmaceutical industries. Volatile organics recovered include alcohols, ketones, esters, glycols, ethers, freons, and specialty solvents. Plant B is able to recover VOCs from still bottoms, coating residues, obsolete paints and inks using thin film evaporators.

At the time of RTI's field visit, a batch consisting of isopropyl alcohol(IPA), xylene, and other VOCs was being processed through the larger ATFE. The reclaimable overhead product was being further purified through fractionation while the bottoms product was maintained at a concentration suitable for offsite fuel use. RTI reports a typical ratio of bottoms product to feed of 1:5. Normally, two passes through the ATFE are used to process this material, with the more volatile IPA removed on the first pass and the less volatile xylene removed on the second pass. However, during this

TABLE 7.2.5. PLANT A: THIN FILM EVAPORATOR WASTE COMPOSITIONS AND HEADSPACE ANALYSIS

	Feed		Product		Bottoms[a]
	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Headspace analysis[b] (mg/L)
Methylene chloride	2.0	1.7	0.9	0.97	0.03
Chloroform	1.5	5.1	ND	0.14	0.01
1,1,1-trichloroethane	0.7	0.11	ND	0.14	0.01
Toluene	1.3	0.01	1.6	0.04	0.03
Mixture of high boiling hydrocarbons	94.4	ND	93.9	ND	ND
Freon TF	ND	0.06	1.8	1.5	0.24

ND = Not Detected.

[a] Bottoms solid upon cooling and no solids analysis was performed.

[b] at 25°C.

Source: Reference 2.

sampling occasion, both IPA and xylene were being recovered on the same pass. Processing conditions were 70°C (158°F) operating temperature and 22 inches of mercury vacuum pressure. Flow rates were not reported. Samples were collected from the feed stream, bottoms product, overhead product, and vacuum pump discharge (gas). A summary of the liquid sample analysis is presented in Tables 7.2.6 and 7.2.7, representing two sampling occasions. The data indicate that the overhead product is more concentrated in volatile species, as expected. However, since no data were presented on the relative volumes of feed, overhead and bottoms streams, removal efficiency cannot be calculated.

7.2.2.4 Thin Film Evaporator - Plant C[2]--

Plant C uses thin film evaporation for the reclamation of organic solvents for recycle or resale as well as for producing specialty solvent blends. The solvent recovery processes include a LUWA ATFE, an SRS Riston Batch Distillation unit and support facilities. The wastes processed by Plant C are from the chemical, plastics, paint, adhesive film, electronics, and photographic industries and include waste chlorinated solvents, freons and ketones. Plant C has no capability for operating the LUWA evaporator under reduced pressure, which precludes processing of high boiling compounds such as naphtha and xylene as overhead products.

The standard recovery procedure is to process each batch of chemicals through the LUWA ATFE during which 70 to 95 percent of the material is stripped off as overhead product.

The ATFE system consists of a 1.0 m^2 (10.8 ft^2) heat transfer surface area evaporator, entrainment separator, condenser, product tank, feed recirculating tank, and pumps. Steam is used as the heating medium with the pressure being set between 207 kPa (30 psig) and 552 kPa (80 psig) depending upon the solvent being processed. The evaporator bottoms are recirculated through the unit until a predetermined VOC removal is reached. RTI reports that the thin film evaporator at Plant C is used in similar applications as reported by Plant A.

During the sampling period, a batch of acetone contaminated with several solvents of concern (see Table 7.2.8) was being processed through the LUWA evaporator. The reclaimed product was being stripped off as overhead and pumped into a product receiver. The bottoms from the evaporator was being

TABLE 7.2.6. ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT B

	Feed No. 1		Feed No. 2		Bottoms[a]
	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Liquid composition (vol. %)	Headspace analysis[b] (mg/L)	Headspace analysis[b] (mg/L)
Isopropyl alcohol	38.2	0.75	42.9	0.69	1.6
Freon TF	0.6	38.	0.5	29.	5.3
Toluene	0.34	0.58	0.3	0.48	0.32
Ethyl benzene	11.4	5.5	10.4	10.4	9.0
Xylenes	49.2	22.	45.7	23.	39.0

[a] Bottoms solid upon cooling and no solids analysis was performed.

[b] at 25°C.

Source: Reference 2.

TABLE 7.2.7. ANALYSIS OF PRODUCT SAMPLES, THIN FILM EVAPORATOR, PLANT B

	Product Sample No. 1		Product Sample No. 2	
	Liquid composition (vol. %)	Headspace analysis[a] (mg/L)	Liquid composition (vol. %)	Headspace analysis[a] (mg/L)
Isopropyl alcohol	53.8	1.1	60.3	1.1
Freon TF	0.7	62.	0.6	51
Toluene	0.4	0.94	0.4	0.71
Ethyl benzene	8.4	5.3	7.0	4.8
Xylenes	34.0	19.	27.4	17.

[a] at 25°C.

Source: Reference 2.

TABLE 7.2.8. **ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT C**

	Feed		Product		Bottoms	
	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)	Liquid composition[a] (vol. %)	Headspace analysis (mg/L)
Acetone	74.3	378.0	82.2	383.0	60.6	308.0
Freon TF	0.1	2.0	<0.1	2.0	0.1	1.5
1,1,1-Trichloroethane	1.5	17.9	2.2	19.1	0.9	9.2
Trichloroethylene	0.2	0.1	0.3	0.1	<0.1	0.1
Toluene	0.5	0.3	0.9	0.2	0.3	0.4
Ethyl Benzene	ND	0.1	0.3	<0.1	<0.1	<0.1
Xylene	5.9	2.1	2.0	0.2	13.6	5.0
Tetrachloroethylene	0.6	2.4	0.5	1.6	0.9	4.1

ND = not detected.

[a] Approximately 17 percent of the waste was high boiling organics and resins.

Source: Reference 2.

pumped back to the feed tank for recirculation through the evaporator. Grab samples of the feed, overhead and bottoms were collected and analyzed with results as summarized in Table 7.2.8.

The following process parameters were provided by Plant C during the field test:

1.	Feed rate (recirculated)	1,635 L/hr (432 gal/hr)
2.	Feed temperature	38°C (100°F)
3.	System pressure	760 torr
4.	Vapor temperature	57°C (135°F)
5.	Steam pressure	310 kPa (30 psig)
6.	Jacket (upper) temperature	132°C (270°F)
7.	Jacket (lower) temperature	107°C (225°F)
8.	Condenser water inlet temperature	20°C (68°F)
9.	Condenser water outlet temperature	25°C (77°F)
10.	Distillate rate	344 L/hr (91 gal/hr)
11.	Bottoms rate (feed-distillate)	1,292 L/hr (341 gal/hr)
12.	LUWA drive motor, amps	1.1

As shown in Table 7.2.8, acetone and other low boiling point compounds were concentrated in the distillate and xylene and other high boilers were enriched in the bottoms. VOCs in the bottoms at the end of the run were not removed to a higher degree because of the requirements to maintain the resins in solution. However, the overall volume of waste was reduced by about 70 percent.

7.2.3 Cost of Treatment

Cost estimates were obtained by GCA[7] and RTI[2] during their case studies to assess ATFEs discussed above. These estimates and those developed by the Pace Company[8] are discussed below.

7.2.3.1 Milsolv Corporation Case Study[7]--

Operating and capital cost data provided by Milsolv enabled GCA to estimate costs of solvent recovery for the three test runs. Table 7.2.9 itemizes operating, maintenance and capital depreciation costs incurred per hour of operation. Assuming an annual production of 940,000 gallons of waste solvent and a capital recovery factor of 17.5 percent, total cost per gallon

TABLE 7.2.9. HOURLY COSTS OF LUWA THIN FILM EVAPORATOR

Expenses	Cost ($/hour)
Fuel	8.00
Auxiliary Chemicals	0.72
Electricity	2.60
Laboratory	9.37
Operating Labor	15.76
Maintenance Labor	14.58
Spare Parts (Repair and Maintenance)	12.69
Regulatory Compliance	6.30
Insurance	0.69
Capital Depreciation	7.27
Total	77.98

In addition to hourly cost, Milsol pays $0.26/gallon to dispose of still bottoms to an incinerator.

Source: Reference 7.

of recovered solvent was calculate' as summarized in Table 7.2.10. As will be noted in a discussion below, the costs are in reasonably good agreement with those derived by Reference 8.

7.2.3.2 RTI Case Studies[2]--

RTI investigators, during their study of ATFEs at three plants, also obtained cost data of varying degrees of completeness. Capital and operating data provided to RTI by Plant A personnel (see Section 7.2.2.2) are summarized in Table 7.2.11. This data is also in good agreement with the results of the Reference 8 study, as discussed below.

7.2.3.3 Cost Estimates Prepared by Pace[8]--

In 1983, the Pace Company generated comprehensive cost data for a variety of solvent recovery technologies, including thin film evaporation. Pace defined a threshold cost of recycled solvent as the cost required to provide various rates of return for a newly constructed recovery system based on a nominal feed rate. Capital cost was divided into three cost components; process equipment, siting and permitting, and engineering and contingency. The methodology adopted here has been described previously in Section 7.1 and uses identical assumptions.

Bottom products were assumed to be 45.5 percent non-solvent (e.g. solids, oil, grease) and cost 54 cents per gallon for disposal. Optimal recovery efficiency and disposal costs will depend on the nature of the waste and ultimate disposal process. These figures represent a compromise between incineration, use as a fuel, and additional solvent recovery costs. If actual disposal costs deviate significantly from this figure (e.g., use as a fuel is typically 20 to 30¢/gal and incineration is $2 to $3/gal) overall treatment cost estimates should be adjusted accordingly.

Labor requirements were assumed to be two employees per hour on-stream at a cost of $14.42 per hour, including overhead. All other operating costs were assumed to be the same as previously presented for distillation. Capital cost estimates are summarized in Table 7.2.12 for ATFEs with three different nominal feed rates. The resulting threshold costs for onsite ATFE recovery are summarized in Table 7.2.13 for varying solids contents, nominal feed rate and percent after-tax discounted cash flow (DCF). Graphical representations

TABLE 7.2.10. PROCESSING COSTS DURING THREE TEST RUNS OF THE LUWA THIN FILM EVAPORATOR

Run # date	Gallons of waste product processed	Time of processing (hours)	Gallons of recovered solvent	Gallons of still bottoms	Operating[a] costs (\$77.98/hr)[e]	Disposal cost of bottoms[b]	Total[c] cost (\$)	Cost per[d] gallon (\$) recovered solvent
1 12/4/85	342	4.25	239	103	331.42	26.78	389	1.63
2 12/3/85	2,835	20.6	1,066	1,769	1,606.39	459.94	2,216	2.08
3 12/5/85	3,910	17.0	1,791	2,119	1,325.66	550.94	2,000	1.12

[a] Operating Costs = $77.98 x Time of Processing.

[b] Disposal Costs of Bottoms = $0.26 x Gallons of Still Bottoms.

[c] Total Cost = Operating Costs + Disposal Cost and Capital Depreciation Cost.

[d] Cost per Gallon Recovered Solvent = Total Cost - Gallons of Recovered Solvent.

[e] See Table 7.2.7 for $77.98/hr figure.

Source: Reference 7.

TABLE 7.2.11. 1984 PLANT A CAPITAL AND OPERATING COST

REPLACEMENT CAPITAL COSTS[a]	
LUWA Evaporator Model LN-0500[b]	$120,000
Main Auxiliaries (Condenser, Pumps, Vacuum System, Controls)	36,000
Piping, Fittings (materials only)	12,000
Structural Frame	6,000
Installation (Foundation, Erection, Piping, Wiring, Insulation)	120,000
Total Installed Cost	$294,000

ANNUAL OPERATING COSTS	
Feed Rate	23 L/min (6 gpm)
Overhead Product, Percent of Feed	85 percent
Operating Labor	$10/hr, $66,000/yr
Maintenance Labor	$25,000/yr
Maintenance Materials	$9,000/yr
Laboratory (1.2 Analysts)	$24,000/yr
Fuel (Steam System, 19 L/hr [5 gal/hr])	$8/hr, $60,000/yr
Electrical (45 hp)	$1.70/hr, $11,000/yr
Cooling Water 1,500 L/min (400 gpm)	$4/hr, $26,000/yr
Overhead	$100,000/yr
Evaporator Bottoms Disposal ($0.05/L [$.22/gal])	$78,000/yr
Schedule Production	310 days/yr
Utilization (88 percent of schedule, 24 hr/day)	273 days/yr

[a] 1984 Cost (per Ray Danaher, LUWA Corporation, July 23, 1984).

[b] 5.00 square meters (53.8 square feet).

Source: Reference 2.

TABLE 7.2.12. CAPITAL COST RECOVERY COMPONENTS FOR ONSITE ATFE RECOVERY SYSTEMS

Nominal feed rate (gph)	Thin film evaporator		
	100	350	500
Process Equipment	126,000	212,900	264,900
Tanks	18,500	37,000	74,000
Subtotal(1)	144,500	249,900	338,900
Engineering, Electrical, Instrumentation (20% of (1))	28,900	50,000	67,800
Subtotal (2)	173,400	299,900	406,700
Contingency 15% of (2)	26,000	45,000	61,000
TOTAL	199,400	344,900	467,700

Source: Reference 8.

TABLE 7.2.13. THRESHOLD COSTS FOR ONSITE ATFE RECOVERY SYSTEMS FOR VARYING SOLIDS CONTENTS AND PERCENT NET DISCOUNTED CASH FLOW (DCF)[a]

Technology	Nominal flow rate (gph)	DCF[b]	Solids (percent)			
			5	10	15	20
Thin Film Evaporator	100	15	0.83	1.02	1.29	1.67
	350		0.39	0.52	0.70	0.96
	500		0.35	0.48	0.65	0.89
	100	30	1.15	1.39	1.72	2.19
	350		0.55	0.70	0.91	1.21
	500		0.50	0.654	0.85	1.14
	100	50	1.59	1.90	2.32	2.92
	350		0.77	0.96	1.21	1.57
	500		0.71	0.89	1.13	1.48

[a] 1982 dollars.

[b] Percent net discounted cash flow.

Source: Reference 8.

of these results (Figures 7.2.7 and 7.2.8), show how threshold costs become increasingly independent of solids content and flow as nominal flow rate increases. This reflects decreasing unit capital and labor costs.

For most onsite facilities, threshold cost will be relatively insensitive to variations in equipment capital costs due to the effects of labor on overall recovered solvent cost. Pace concluded that a threshold change of only plus or minus 5 percent may result from capital cost fluctuations of 20 per cent . However, cost will be sensitive to changes in on-stream time (capacity factor). This is illustrated in Table 7.2.14 for the case of constant labor (2 employees) and increasing labor with run time. Cost of recovery is highly sensitive to labor costs, particularly for small units, and equipment utilization as shown.

If the solvent recovery equipment were operated less than 40 hours per week, threshold costs could increase dramatically due to increased fixed cost per gallon recovered. For example, cost per gallon for a 100 gph unit jumps from $1.02 to $1.38 if the unit is operated only 50 percent of the time ($2.10 at 25 percent utilization). Assuming a minimum of two people are required to operate a ATFE system, significant cost savings could not be expected by using a 50 gph system since labor costs will compensate for much of the reduced capital cost. Instead, low utilization rates may result in more economical processing offsite or through some combination of onsite distillation and offsite recovery of still bottoms. Offsite recovery is discussed in Section 3.4. In general, offsite facilities incur additional fixed costs (e.g., transportation, permitting, siting, boiler and lab facilities) relative to onsite recovery systems. However, these costs are offset by their high volume capability.

7.2.3.4 Cost Comparisons Between Pace and Site Visit Reports--

A rough comparison of the Pace cost estimates can be made with the case studies presented earlier that were performed by GCA and RTI. Using cost data supplied by Milsolv to GCA personnel (Tables 7.2.9 and 7.2.10), ATFE processing costs can be compared with estimates derived from Figure 7.2.7. With an average feed rate of 169 gph at 9.2 percent solids Pace estimates processing costs of approximately $0.85 per gallon recovered compared to $1-$2 as reported by Milsolv. The major difference in the cost figures is accounted

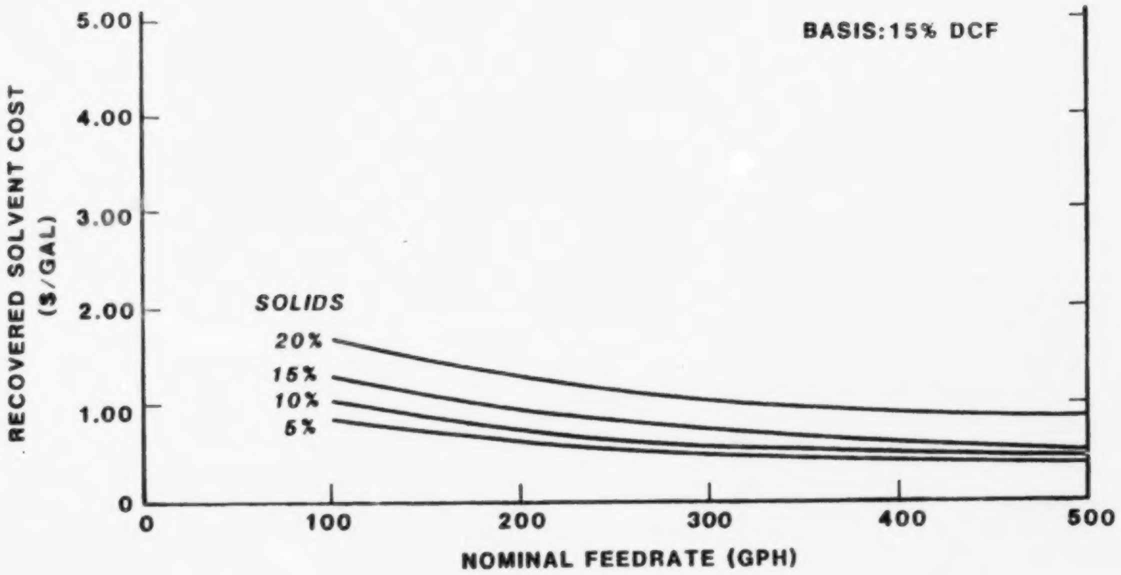

Figure 7.2.7. Threshold costs for onsite ATFE versus feed solids concentration.
Source: Pace, Reference 8.

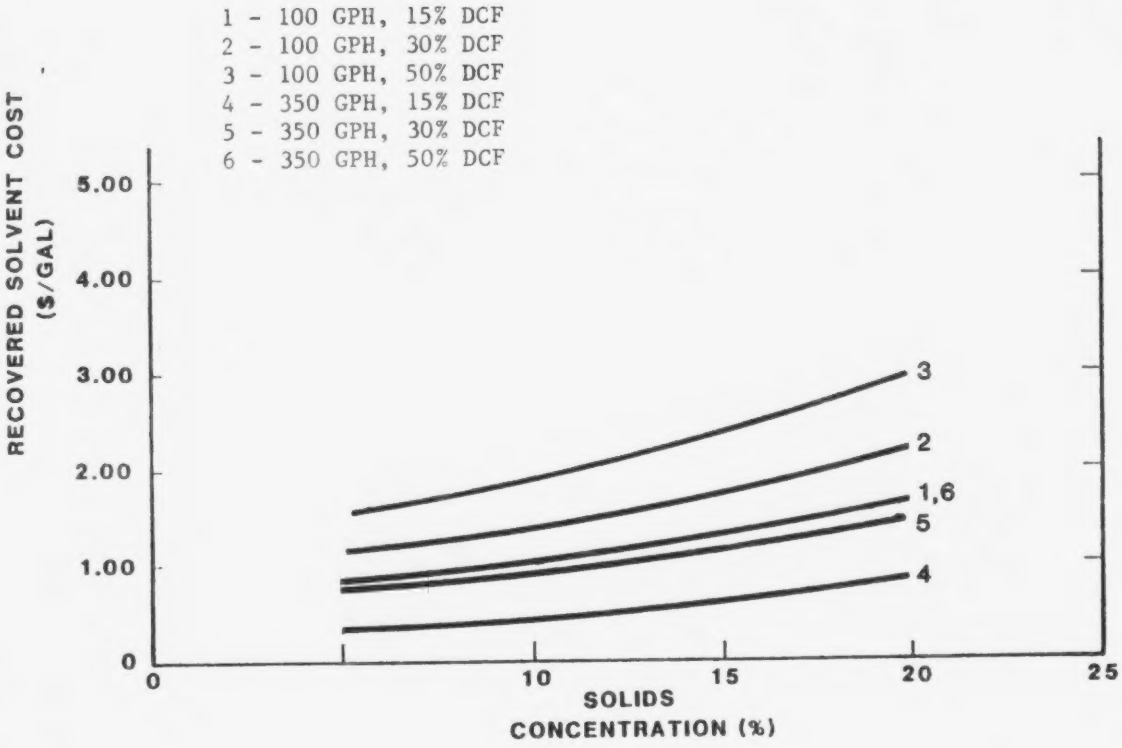

Figure 7.2.8. Threshold cost vs. feed solids concentration for solvent recovery using ATFE.

Source: Pace, Reference 8.

TABLE 7.2.14. THRESHOLD COSTS FOR ONSITE SYSTEMS VERSUS CHANGES IN CAPACITY FACTOR (Recovered Solvent)[a]

BASIS: 2,080 hours base nominal run time

10% solids

15% discounted cash flow (after taxes)

Nominal feed rate (gph)	Number of persons (labor)	Run time (hours)	Constant labor ($/gal)	Variable labor ($/gal)
100	2	2,000	1.02	1.02
	3	3,000	0.77	0.91
	4	4,000	0.63	0.84
	5	6,000	0.49	0.70
500	2	2,000	0.48	0.48
	3	3,000	0.39	0.42
	4	4,000	0.35	0.39
	5	6,000	0.30	0.34

[a] 1982 dollars.

Source: Reference 8.

for by a higher projected recovery rate by Pace (80% overhead) versus that reported by Milsolv (44% overhead). Milsolv generated bottoms which are blended as fuel at \$0.26/gal while Pace's estimates provide far more complete recovery and higher bottoms disposal cost (\$0.54/gal). If costs were based on feed rate as opposed to overhead rate, Pace's estimate becomes \$0.68/gal versus \$0.66 based on Milsolv's figures.

Substituting figures provided through RTI's interviews with Plant A personnel (Table 7.2.11)[2], processing costs were approximately 20¢/gal of recovered product based on the capital depreciation schedule and land use costs suggested by Pace for commercial facilities.[8] Pace's figures result in an estimated 40¢/gal when the ATFE is assumed to account for 50 percent of the facility's fixed costs. This figure is higher primarily because of the increased disposal cost (54¢/lb of bottoms versus 22¢ reported by Plant A) and labor costs assumed in the Pace analysis. Overall costs from both estimates are low due to high utilization (6,473 hours per year) and high recovery rate (87.5 percent). Energy consumption (4¢/gal) and LUWA purchase and installation cost (\$294,000) were in good agreement.

Specific operating and capital costs were not discussed for Plant B primarily because of the diversity of process systems at this facility. In addition, processing costs depend upon the particular feed stream being processed and the intended use of the product. However, Plant B personnel did state that it would not be economical to recover waste streams with less than 6 to 8 percent reclaimable organics. They provided additional processing information as follows:

- Processing costs are approximately \$1/gal when organic is stripped as the overhead product.
- Processing costs are approximately \$1.50/gal when water is stripped overhead with the organic becoming the bottoms product.
- The installed cost of a new 5.76 m^2 (62 ft^2) Votator thin film evaporator system would be about \$300,000.
- The cost of shipping ATFE bottoms to a cement kiln are approximately 20 to 30 cents per gallon.

Thus, capital equipment and processing costs ($1.00/gal) are in general agreement with estimates provided by Pace for solvent reprocessing facilities ($0.61/gal).[8]

Cost data from Plant C was not detailed enough to make any meaningful comparison with other data.

7.2.4 Overall Status of Process

7.2.4.1 Availability--

ATFEs are widely used in a number of industries including the solvent recovery industry due to their unique ability to process viscous wastes relative to other evaporation/distillation technologies. Evaporators and accessory equipment can be obtained from a number of manufacturers in various sizes and configurations. Ten firms are identified as suppliers of the ATFE in the 1986 edition of McGraw-Hill's Chemical Engineering Equipment Buyers' Guide.[9] Major producers include Blaw-Knox (Buffalo, NY), Cherry Burrell (Louisville, KY), LUWA (Charlotte, NC), Kontro (Orange, MA), Pfaudler (Rochester, NY) and Artisan Industries (Waltham, MA).[2]

7.2.4.2 Application--

Evaporators can be used to recover solvents and other volatile organics from both organic and aqueous waste streams provided the treated waste does not exceed viscosity limits imposed by the system design (see Table 7.2.1) and operating temperature. Excessive solids content will increase viscosity and foul heat transfer surfaces. Therefore, some pretreatment for gross solids removal may be required.

In practice, recovery to low residual organics is limited by viscosity due to increased resistance to mass transfer. This resistence is partially offset in an ATFE due to the high turbulence generated in the vessel. Recovery is also limited by operating pressure since this pressure determines the equilibrium concentration of solvent remaining in the waste. Finally, recovery of organics from waste streams may not be economical unless the recoverable organic content is greater than 6 to 8 percent.[2] A rough cost analysis based on solvent purchase and disposal costs supports this figure.

However, wastes with recoverable solvent concentrations of as little as 3 to 5 percent may be profitably recovered when processed in existing, high volume onsite facilities which are underutilized.

ATFEs are likely to find more widespread use relative to conventional distillation equipment. Land disposal restrictions and limitations on halogen content in supplemental fuels will compel recyclers to pursue higher recovery rates when processing waste halogenated solvents.

7.2.4.3 Environmental Impacts--

In selecting evaporators as a treatment technology it should be recognized that, except in isolated cases, further treatment of the bottoms stream will be required to meet EPA land disposal or NPDES discharge requirements. Air emissions from the overhead condenser have been identified as a potentially significant source of VOC emissions by RTI.[2] VOC concentration averaged 41.1 mg/l in Plant A and 34.4 mg/l in Plant B at the vacuum pump outlet. However, no estimates of total release of emissions factors were provided. Emission rate would be greatest during process start-up. They would increase if air was leaking into the system, noncondensible gases were being formed or if the condenser became overloaded. Vacuum pump emissions controls should be examined as a potential additional cost since treatment requirements (e.g., carbon adsorbers) may be necessary to avoid adverse environmental impacts.

7.2.4.4 Advantages and Limitations--

Evaporation, as a means of recovering useful solvents and other low boiling organic materials, is a common unit operation used by a variety of industries. It also finds application in removing water from viscous, non-volatile fluids. The ATFE units most significant advantage compared to other recovery processes is its ability to handle viscous liquids. However, its cost must be compared with that of less expensive, conventional recovery technologies (e.g., distillation) and their associated residual treatment costs; e.g. thermal destruction, solidification, and land disposal. The cost of the entire treatment train will ultimately dictate selection of the optimal recovery technique.

Limitations arise from the need to follow evaporation processes with other treatment technologies in order to eliminate bottoms stream and, possibly, vapor phase residuals.

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7.3 STEAM STRIPPING

7.3.1 Process Description

Steam stripping is used in both industrial chemical production and waste treatment to remove gases or volatile organic chemicals from waste streams by injection of steam into a tray or packed distillation column. This unit operation is most effectively applied in aqueous solutions for the removal of volatile components that are immiscible in water. It can also be used for stripping organic solutions when water forms low boiling azeotropes and does not adversely affect overhead or bottoms quality. The presence of water must either be acceptable or economically separated to achieve product purity specifications.

Steam stripping is commonly employed to separate halogenated and certain aromatic compounds from water, but is less effectively used to recover miscible organics such as ketones or alcohols. It is preferable to conventional distillation processes for recovering high yields of contaminated wastes which would otherwise foul heat transfer surfaces. It is also more economical and effective at recovering wastes with high concentration of volatiles and wastes with low volatility when compared to air stripping.[1]

Figure 7.3.1 illustrates a typical steam stripping process. Waste enters near the top of the column and then flows by gravity countercurrent to steam. As the waste passes down through the column it contacts vapors rising from the bottom of the column that contain progressively less volatile organic compounds. The concentration of volatile compounds in the waste reaches a minimum at the bottom of the column where it is discharged. The overhead vapor is condensed as it exits the column and the condensate is then decanted to achieve solvent/water separation. Reflux may or may not be used, depending upon the desired composition of the overhead stream.

The common uses for steam distillation can be summarized as follows[2]:

1. To separate relatively small amounts of a volatile impurity from a large amount of material.
2. To separate appreciable quantities of low solubility, higher-boiling materials from nonvolatile wastes when the materials to be separated form low boiling azeotropes with water.

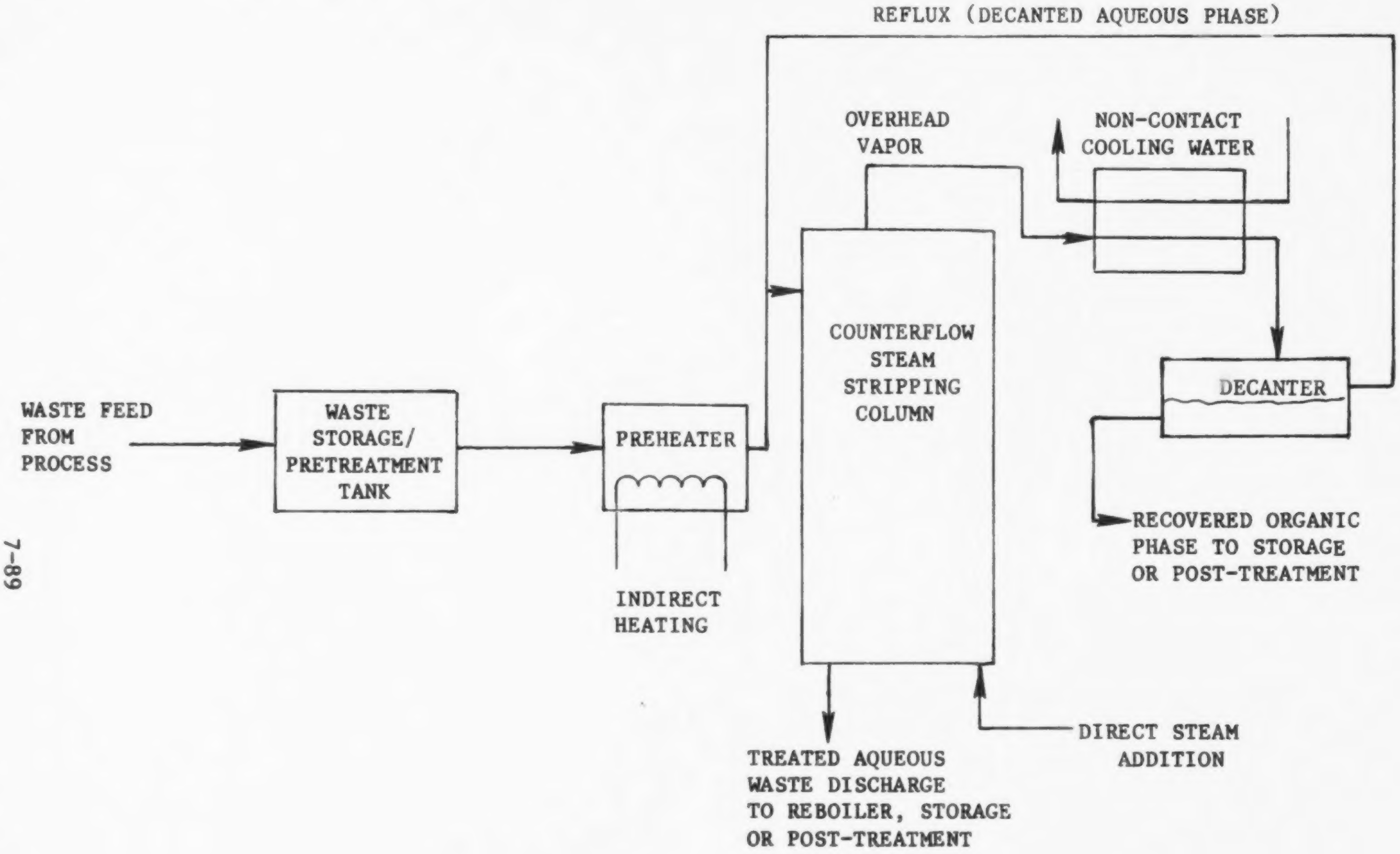
REFLUX (DECANTED AQUEOUS PHASE)
OVERHEAD VAPOR
NON-CONTACT COOLING WATER
WASTE FEED FROM PROCESS
WASTE STORAGE/ PRETREATMENT TANK
PREHEATER
COUNTERFLOW STEAM STRIPPING COLUMN
DECANTER
RECOVERED ORGANIC PHASE TO STORAGE OR POST-TREATMENT
INDIRECT HEATING
DIRECT STEAM ADDITION
TREATED AQUEOUS WASTE DISCHARGE TO REBOILER, STORAGE OR POST-TREATMENT

Figure 7.3.1. Typical Steam Stripping Process.

3. To recover material which is thermally unstable or reacts with other waste components at the boiling temperature.

4. To recover material which cannot be distilled by indirect heating even under low pressure, because of the high boiling temperature.

5. To recover material in instances where direct-fired heaters cannot be used because of ignition or explosion hazards.

Theoretical Considerations--

The residual streams from steam stripping of aqueous wastes typically consist of decanted overhead products and treated waste stream bottoms. The stripped waste is sewered or undergoes additional treatment as necessary to further reduce contaminant levels; e.g., carbon adsorption. Depending on required purity, decanted solvent is either used directly or further purified; e.g., drying, fractionation. The overhead aqueous phase is typically returned to the stripping column if even a slight solubility exists between water and the organic components.

The use of steam in distillation permits a more complete separation of immiscible liquids at lower temperatures for the same conditions of total pressure or vacuum. The essential feature of an immiscible system is that each liquid phase exerts its own total vapor pressure, regardless of the quantity of the other liquid phase. At constant system pressure, the presence of steam reduces the total vapor pressure from the liquids which is required to induce boiling, thereby lowering system temperature requirements. This permits separation of compounds which could not be accomplished through conventional distillation due to polymerization (e.g., pyridine, cresols, monomers) or thermal decomposition (e.g., halogenated solvents) of waste constituents.

With the exception of certain acids, most organic compounds produce minimum boiling azeotropes with water. This phenomena is characteristic of mixtures with dissimilar molecular species with activity coefficients greater than unity. As can be seen in Appendix A, most solvents and ignitables fall into this category.

A minimum boiling azeotrope forms at a temperature below that of the boiling point of the pure compounds. Unless this azeotrope is shifted to more favorable equilibrium conditions through lowering operating pressure or addition of a chemical complexor (entrainer), it will act as the limiting concentration which can be achieved in the overhead product. With some organic mixtures, water can act as an entrainer to preferentially distill compounds by creating a low boiling azeotrope.

As compounds become more dissimilar, they tend to approach liquid immiscibility (e.g., chlorinated solvents or aromatics in water). Their equilibrium vapor concentration will be essentially constant over an increasing range in liquid concentrations and only begin to deviate from this level at very high or very low liquid concentration. Generally, the azeotrope will occur within the liquid immiscibility composition range forming a heterogeneous overhead product which can easily be separated into two phases. Examples clarifying this and other concepts are provided below.

Water and 1,1,2-trichloroethane, two slightly miscible liquids, boil at 86°C (1 atm) to form a heterogeneous azeotrope consisting of 83.6 percent 1,1,2-trichloroethylene. The normal boiling point of 1,1,2-trichloroethylene (113.7°C), is substantially higher than the azeotropic boiling point, thus heating costs are reduced in the presence of steam. The overhead product readily separates into two phases, the upper layer consisting of 99.55 percent water and the lower layer consisting of 99.95 percent 1,1,2-trichloroethylene (specific gravity = 1.443)[3]. Thus, steam distillation is readily applied to this compound, particularly if it must be removed from polymerizable, nonvolatile material which can foul distillation equipment at the normal boiling point.

Steam stripping is also effective in instances where water acts as an entrainer to shift the vapor-liquid equilibrium toward more desirable conditions. For example, mixtures can shift toward higher concentrations of the less ionic component in the overhead product in the presence of steam. Benzene-alcohol overhead products resulting from steam stripping will be more highly concentrated with benzene relative to normal distillation and will separate into two phases upon condensing (e.g., benzene and isopropanol/water), thereby further concentrating the components.[3] A summary of azeotrope data for solvents and ignitables was presented previously in Table 7.1.1. Additional information regarding azeotrope theory and azeotropic and extractive distillation can be found in standard engineering texts.[4,5]

In the absence of azeotrope data for wastes, the principal indices used to predict steam stripping feasibility are boiling point and Henry's Law constant. Compounds with boiling points less than 150°C (i.e., volatile compounds) have good steam stripping potential, as do compounds with Henry's Law constants greater than 10^{-4} atm-m^3/mole.[6] The constant expresses the equilibrium distribution of a compound between air and liquid for dilute solutions. It is roughly proportional to the product of vapor pressure and the reciprocal of solubility, thus taking into consideration the miscibility of the compound in the liquid phase. Therefore, increasing value of the Henry's Law constant also correlates with increasing favorability of volatilization through the use of steam stripping.

It should be noted, however, that a study performed by the U.S. EPA/OAQPS[1] suggested that the use of Henry's Law constants given in the literature for some chemicals could result in underestimating the required contact time and overestimating the removal efficiency of steam stripping. As part of the study, Henry's Law constants were calculated from headspace and liquid composition sampling data. These calculated constants were substantially less than their corresponding literature values, but did provide good correlation with test data. It is recommended that vapor-liquid equilibrium data be established through headspace analysis and activity coefficient models for more complex solutions.[1] Alternatively, relative volatilities in non-ideal situations can be modeled through the use of partition coefficients and critical constants.[7]

7.3.1.1 Pretreatment and Post-Treatment Requirements--

Certain waste characteristics will determine the viability of steam stripping as a waste treatment technique. Restrictive waste characteristics include:[11]

- High solubility of the organic compound in water; usually more than 1,000 ppm;
- Organic compounds with high boiling points (more than 150°C);

- VOC concentration in excess of 10 percent; above this concentration, distillation may be more cost effective; and

- Suspended solids concentration in excess of 2 percent or materials that tend to polymerize at operating temperatures; these can cause fouling of packing material and eventual plugging of equipment.

Pretreatment requirements for wastes therefore consist of reducing high concentrations of volatiles, solids, and polymerizable organics. Highly concentrated volatile wastes are more economically pretreated through conventional evaporation/distillation technologies. The diluted bottoms product can then be treated via steam stripping. Alternatively, chemical oxidation pretreatment can convert polymerizable and miscible wastes to more inert and less soluble forms.

Solids, metals, oil and grease concentrations can be reduced through a variety of pretreatment techniques as discussed in Section 6.0. These include precipitation, coagulation, floculation, centrifugation, membrane separation processes, flotation and other chemical/physical separation processes. For example, fouling of packing material with oxidized iron and manganese can be reduced through pretreatment via lime precipitation. Membrane separation processes are effective in removing high molecular weight compounds. Since these compounds are typically nonvolatile, and thus not ammenable to steam stripping, pretreatment methods using membrane separation techniques compliment steam stripping removal efficiency while reducing column fouling. High solids removal in pretreatment steps also enables higher solvent recovery rates since often times maintaining a pumpable bottoms product is the limiting factor in solvent recovery.

Post-treatment is generally required of both the overhead and bottoms stream, although data show that steam stripping may be capable of reducing solvent concentration in wastewater bottoms streams to levels which meet the land disposal ban treatment standards. However, due to economic considerations, conventional wastewater treatment methods (e.g., adsorption, air stripping, biological or chemical treatment) are more commonly employed to remove residual organic levels from aqueous streams.

Concentrated organic bottoms such as oily wastes and low volatility, organic sludges must be separated from the condensed steam through decanting, centrifugation, and other physical separation techniques. Overhead products undergo liquid-liquid separation, typically through decanting followed by dehydrating of the recovered solvent. Depending on its solvent levels, the decanted aqueous stream is reprocessed through the stripper or treated via other wastewater treatment processes. Alternatively, it could be used along with a portion of the stripped wastewater bottoms to generate steam if the boilers are properly equipped to accommodate the presence of volatile components.[10]

7.3.1.2 Design Characteristics and Operating Parameters--

Stripping towers operate in a batch or continuous mode. Generally, batch stripping is of less commercial interest and is reserved for low volume processing or for staged stripping of streams with multiple volatile components which have different boiling points. Continuous operation more effectively separates components of comparable volatility, provides higher purity of separated products and uses less stripping medium for the same degree of separation, particularly when stripping to low levels of organics.[2]

Three modes of flow are possible: cocurrent, countercurrent, and crossflow. Cocurrent flow, being least efficient, is not usually used, while crossflow operation is often preferred to counterflow since it provides greater transfer efficiency over a wider operating range.

A tower can be operated isothermally or adiabatically. Steam stripping is typically performed isothermally; i.e., temperature is constant along the length of the tower. The feed is usually preheated to the boiling point before entering the tower to minimize steam requirements and, consequently, treated waste volume.

Reflux involves condensing a portion of the vapors from the top product and returning it to the tower. This can enhance separation by increasing the concentration of the stripped organics in the vapor stream. This occurs because condensation of vapor in the column is required to heat the refluxed liquid to its bubble point. This increases the concentration of strippable components in the liquid stream which, in turn, will increase their equilibrium vapor concentrations. This effect will be most important as the solution components become more miscible in one another.

Similarly, for miscible fluids, introducing the feed at a lower tray in addition to refluxing can increase the concentration of organics beyond that obtainable by reflux alone. Addition of reflux shifts the distribution in the column from rectifying to stripping zones. A column designed with variable feed plate location can accommodate this shift, as well as changes in waste feed to permit column operation at maximum efficiency.

The optimal size of the rectifying zone depends on the waste being treated. If feed enters at the top of the column (i.e., no rectifying zone), the limiting overhead concentration is given by the vapor equilibrium with the feed. As the rectifying zone is increased, the overhead concentration is similarly increased and approaches the azeotropic concentration limits.

Finally, stripping can be carried out in two types of towers. Tray towers provide staged contact between the liquid and vapor streams. Alternatively, packed towers can be used which allow for continuous contact between the two phases. Packed towers are less expensive, have low liquid hold-up, low pressure drop, and are preferred for low pressure operation and treatment of corrosive, foaming or viscous liquids.[8] However, tray columns have been more widely used in the past and consequently are more predictable in their performance. Tray columns are more flexible in that they operate efficiently over a wide range in flow rates and can readily be adapted to process multiple feeds or sidestreams.[8] They are also more easily cleaned and are, therefore, preferred for processing wastes with high concentrations of metals, solids, or polymerizable materials. Selection of packed versus tray towers has been discussed in more detail in Section 7.1.

Steam stripper design will ultimately be dependent on the waste characteristics, throughput, and desired residual characteristics. Thus, tower height, diameter, packing material and bed volume (or type and number of trays), materials of construction, and use of ancillary equipment (e.g., reflux, heat exchangers) are highly specific to the waste being treated. For example, a survey of commercial steam strippers currently in use to treat pollutants revealed tower diameter ranges of 1.0 to 9.5 feet, column height ranges of 10 to 180 feet, and throughputs ranging as high as 500,000 GPD.[8]

In typical applications of stripping volatiles from aqueous wastes, steam requirements range from 10 to 30 mole percent of the feed at system pressure of 1 atm and 100°C.[9] Steam consumption is directly related to the equilibrium vapor pressure of the material being stripped and the resistance to diffusion of the compound through the waste. The latter determines the extent to which equilibrium conditions are approached and becomes increasingly important as the concentration of volatile species is diminished. Equipment manufacturers provide steam consumption data for stripping organic streams (e.g., degreasing solvents) which are appropriate if significant solvent quantities remain in the bottoms product. For example, one manufacturer reported 1,236 lbs/hr of steam required to steam distill spent mineral spirits in a 100 gph capacity still. Processing xylene on the same unit would require 829 lbs/hr whereas toluene steam requirements would be only 419 lbs/hr.[10]

Steam strippers are generally custom designed for specific applications. Conversely, steam injection stills include modified pot stills and low volume packaged units. These have throughput ranges of 10 gallons/hour or less and are available in portable skid-mounted designs. However, despite this versatility in design, in practice steam strippers are limited to the extent that they can recover solvent wastes.

For compounds which form minimum boiling azeotropes, purity of the bottoms product is limited by the equilibrium liquid phase mole fraction which, in turn, is limited by economic considerations. Commercially available distillation systems have lower operating pressure limits due to the increased costs associated with maintaining a vacuum and condensing overhead product at temperatures below the range of air or water cooling.

A given pressure (typically atmospheric) defines the temperature required to boil a mixture. As the liquid mole fraction of the stripped component decreases in the bottoms product, the temperature required to continue stripping approaches the boiling point of the remaining liquid. If thermal decomposition or polymerization can occur, temperature as well as pressure limitations may restrict attainable degree of separation. Otherwise, economic factors associated with capital costs of the column can make post-treatment alternatives (e.g., activated carbon) more attractive as methods to separate residual contaminant levels from the bottoms stream.

As the initial liquid concentration approaches that of the equilibrium vapor concentration, the utility of steam distillation as a concentration technique is reduced. Conversely, compounds which form azeotropes at weight fractions significantly above the weight fraction in the untreated waste are good candidates for concentration through steam stripping, particularly if the compound is volatile. More soluble compounds will only be ammenable to steam stripping if they are highly volatile.

The reader is referred to design methodologies and cost estimation procedures which have been developed in the literature for more information on steam stripping design, optimization, and cost effectiveness.[1,2,4,5,9]

7.3.2 Demonstrated Performance

The results of a number of different case studies, both pilot-scale and full-scale, are presented in this section. Each subsection addresses the results of a specific study. The first two cases involve full-scale batch steam distillation of organic wastes at solvent recovery facilities. These are followed by summaries of performance data characterizing operation of 13 industrial scale, continuous flow steam strippers treating solvent contaminated wastewater streams. Finally, results from two laboratory scale steam stripping studies are summarized. These studies were conducted to design full-scale units for treating petrochemical processing wastes and ground water which was heavily contaminated with solvents.

Steam Injection Still--

GCA conducted a performance evaluation of a steam injection still operated by Environmental Processing Services (EPS) of Dayton, Ohio in October, 1985.[12] The roughing still employed by EPS to treat halogenated solvent wastes is a direct steam injection batch still which is operated at atmospheric pressure. Initially, three drums of waste solvent are pumped into the still with another drum of solvent waste added approximately once every half hour. As the run progresses, temperatures in the still increase from just over 100°F and approach the boiling point of water (212°F). Attainment of this temperature indicates that most of the solvent has been removed. After ten drums are processed, still bottoms are discharged to a holding tank from which they are shipped offsite for use as a supplemental fuel in a cement kiln.

Steam supplied by an existing onsite boiler is injected directly into the solvent waste. As the solvent is heated by the steam, water and solvent vaporize, pass through a condenser, and are discharged to a coalescer. The decanted water layer is discharged to the sewer and recovered solvent is sent through a polishing still for final treatment.

A mixed stream of spent 1,1,1-trichloroethane was processed during the sampling period. Processing data are summarized in Table 7.3.1. A total of ten drums were processed in 264 minutes, yielding an average feed rate to the batch unit of 2 GPM. A recovery rate of over 90 percent was reported for 1,1,1-trichloroethane. Processing of this waste stream was limited to the extent required to generate a bottoms product which was acceptable as a cement kiln fuel substitute; e.g., Cl content of roughly 3 percent.

GCA collected samples of the 1,1,1-trichloroethane waste feed, still bottoms, solvent overhead product (from the polishing still), and the sewered water phase which was separated in the coalescer. These streams were sampled for 1,1,1-trichloroethane and metals as summarized in Tables 7.3.2 and 7.3.3, respectively. As shown, 1,1,1-trichloroethane concentration in the bottoms product was significantly reduced with overall solvent recovery exceeding 90 percent. Solvent concentration in the sewered aqueous stream was 6 percent which indicates that this stream should have been subjected to additional treatment.

Some metals were concentrated in the bottoms product from 4 to 7 times greater than levels found in the waste feed. In particular, lead was present in high enough concentration (14 ppm) in the still bottoms so that it may fail the EPA toxicity test. The presence of metals in the overhead products indicate some carry-over of these products with the distillate. Zinc, copper, lead and chromium were present in these streams in significant concentrations.

The still bottoms were also analyzed for fuel value. The overall heat content was 14,240 Btu/lb with a viscosity of 38 SSU (at 100°F), ash content of 0.05 percent, sulfur content of 0.56 percent, and nitrogen content of 0.04 percent. GCA noted that removal of the lower phase (85 percent water) could significantly increase the fuel value of this residual stream.

TABLE 7.3.1 PROCESS DATA FOR THE STEAM DISTILLATION UNIT

Run Number	4
Date of Test	10/29/85
Waste Description	1,1,1 Trichlorethane waste solvent coming from several generators.
EPA Waste Code	F001
Number of drums processed during test (55 gals/each)	10
Length of test period (minutes)	264
Process Rate (gal/min)	2.1[a]
Temperature (°F)	212[b]

[a] 10 drums were processed in 264 minutes. The feed rate is not constant. Initially 3 drums are pumped into the unit in about 15 minutes. About once every hour another drum is added (takes about 3 minutes to pump entire contents of a drum) to the still after sufficient solvent has been distilled.

[b] Over the course of the run the temperature gradually increases until the boiling point of water is reached.

Source: GCA. Reference No. 12.

TABLE 7.3.2 PERCENT BY WEIGHT OF 1,1,1-TRICHLOROETHANE IN THE WASTE STREAMS DURING OPERATION OF THE STEAM DISTILLATION UNIT

	Upper phase	Single phase	Lower phase
Waste Feed	5.0[a]		92.0
Still Bottoms	2.8[b]		4.4[c]
Solvent Product		89.0	
Roughing Still Water		5.5	

[a] Primarily water (49.6%) and contaminants such as solids and oils.

[b] Primarily oil and Solids (0.14% water)

[c] Primarily water (85.7%)

Source: GCA. Reference No. 12.

TABLE 7.3.3 METAL ANALYSES FOR THE STEAM DISTILLATION UNIT (μg/g)

Metal	Waste Feed			Still Bottoms	Roughing Still Water			Solvent Product
	1	2	3		1	2	3	
Ag	<0.08	<0.08	<0.08	<0.09	0.02	<0.01	0.02	0.004
As	<0.32	<0.33	<0.32	<0.36	<0.04	<0.04	<0.04	<0.013
Be	0.0080	0.12	0.008	0.060	<0.0005	<0.0005	<0.0005	<0.0003
Cd	0.057	0.074	0.065	0.404	<0.002	0.002	0.003	<0.0006
Cr	0.607	0.885	0.454	4.57	<0.003	<0.003	<0.003	0.016
Cu	3.5	4.3	4.0	17	0.31	0.35	0.32	0.014
Ni	0.348	0.442	0.333	1.93	<0.006	<0.006	<0.006	0.006
Pb	7.7	3.7	4.8	14	0.12	.011	<0.12	0.006
Sb	<0.40	0.82	<0.40	0.98	<0.05	<0.05	<0.05	<0.016
Se	<0.32	<0.33	<0.32	<0.36	<0.04	<0.04	<0.04	<0.013
Tl	<0.24	<0.24	<0.24	<0.27	<0.03	<0.03	<0.03	<0.010
Zn	15.8	20.2	18.2	132	0.315	0.320	0.294	0.004

Source: GCA. Reference No.12.

Finally, the extent of volatile release from the process was determined by taking OVA measurements (readings were in methane equivalents) during the 264-minute run. Sampling locations included directly above the coalescer and near the two exits in the room where the unit was located. The highest recorded emissions were 30 ppm above the coalescer, but levels dropped to less than 20 ppm at the room exits (this probably includes compounds other than 1,1,1-trichloroethane).

The data indicate that significant recovery is achievable in steam-injected stills. Mixed chlorinated waste, containing approximately 30 percent solvent contaminated with oil, water and solids, was processed to yield over 90 percent solvent recovery while generating a fuel bottoms product. However, a metals analysis on the bottoms showed levels of toxic compounds (lead, chromium) which were comparable to levels found in waste oil. These could represent a health hazard if burned in boilers which are not equipped with particulate emission controls.

Full-Scale Steam Distillation (Stripping)--

Research Triangle Institute (RTI) and Associated Technologies, Inc., under contract with the EPA, collected field data at a hazardous waste facility, "Plant D", to evaluate the performance of a batch steam stripping unit used to recover solvents from waste.[13]

The contaminated organics processed by Plant D are generated mostly by the chemicals, paint, pharmaceutical, plastics, and heavy manufacturing industries. The types of chemicals recovered include ketones, aromatic hydrocarbons, chlorinated solvents, Freons, and petroleum naphthas. Generally, 50 to 70 percent of the waste consists of recoverable solvent which is returned to the generator or marketed to suitable end users. Aqueous residues from the stripping process are either sewered or solidified by mixing with sorbents and landfilled. Organic residues are typically incinerated.

The steam stripping system, consists of a 250-gallon batch stripping vessel equipped with a steam sparger, overhead vapor condenser, distillate receiver and decanter, a miscible solvent tank, product storage tanks, a residue tank, and associated pumps and support facilities.

A typical 250-gallon batch can be processed in one hour. Most solvents handled by the facility are relatively immiscible with water and decant readily. The aqueous phase from the decanter is collected in a miscible solvent tank (MST) to be reprocessed through the stripper for recovery of residual solvent. In many cases, the stripped aqueous phase is then suitable for discharge to the municipal wastewater treatment system.

Four batches of wastes were evaluated: an aqueous xylene waste (Batch 1), a chlorinated organic-oil mixture (Batch 2), a chlorinated organic-water mixture (Batch 3), and a mixture of solvents and water (Batch 4). Waste characterization data for these batches is summarized in Table 7.3.4. Processing data is summarized in Table 7.3.5. Steam stripping of all batches was discontinued when the vapor temperature reached 211°F. to avoid excessive water in the overhead product.

Batches 1, 3, and 4 were two-phase liquid systems with the organic phase ranging from 3 to 19 percent by weight. After steam stripping, the bottoms were reduced to a single-phase aqueous product with volatile organic constituent (VOC) concentrations ranging from 391 to 12,031 ppm. VOC removal efficiencies ranged from 93.7 to 99.8 percent.

Batch 2 was a solvent-oil mixture with an initial VOC content of 74 percent by volume. This was stripped to 0.41 percent VOC (99.5 percent removal efficiency) yielding an oil-water bottoms product.

Steam requirements varied considerably depending on the batch volume, latent heat, heat of vaporization, and heat transfer efficiency. Direct steam injection was used to heat the waste to its boiling point. This results in maximum steam consumption and water concentration in both the overhead and bottoms products. The ratio of steam consumption to recovered VOCs was lowest for the organic waste (Batch 2) and highest for the least concentrated stream (Batch 4) as shown in Table 7.3.5.

RTI also presented data for headspace and liquid VOC concentrations as a function of stripping time. However, these data are incomplete for the three multiphase batches, since the organic phases were not fully characterized. Thus, strictly speaking, stripping rate constants can only be meaningfully discussed for Batch 2.

TABLE 7.3.4. PLANT D: CHARACTERIZATION OF WASTES

	Batch 1	Batch 2	Batch 3	Batch 4
Number of phases	2	1	2	2
Total solids (mg/L)	880	2,800	130	130
Water (weight %)	81.3	Negligible	82	97
Oil (weight %)	Negligible	19.9	Negligible	Negligible
VOC (weight %)	18.7	80.1	18.0	3.1
Density (g/cm^3)	1.0[a], 0.866[b]	1.2[d]	1.0[e]	1.0
VOC Analysis (influent/bottoms)				
Aqueous phase (mg/L)				
Acetone	39/<6	-	290/<6	6,500/ 6
Isopropanol	960/<6	-	37/<6	95/-
Methyl ethyl ketone	1,040/34	-	320/<7	112/-
1,1,1-Trichloroethane	170/20	-	180,000/12,000	2,200/230
Tetrachloroethene	290/<20	-	-	55/-
Ethyl benzene	360/100	-	44/12	-
Toluene	86/42	-	-	170[f]/35
Xylene	2,000/270	-	-	900[f]/120
Organic phase (weight %)				
Xylene	70.0/0	-	-	-
Methyl ethyl ketone	-	75,000/ 7[c]	-	-
1,1,1-Trichloroethane	-	660,000/4,100[c]	<100/0	-
Xylene and toluene	-	-	-	<100/0
Miscellaneous organics	30.0/0	>0	>0/0	>0/0

[a] Aqueous phase.
[b] Organic phase.
[c] mg/L
[d] Estimated from pure components.
[e] Estimated as density of water.
[f] Values reported here are concentrations reported after 10 minutes of stripping. Actual measured values were: toluene - 86 mg/L; to xylene - 4 mg/L. These were low due to incomplete mixing when the feed sample was collected.

Source: Adapted from RTI - Reference No. 13.

TABLE 7.3.5. PLANT "D" BATCH STEAM STRIPPER: PROCESS DATA[a]

	Batch 1	Batch 2	Batch 3	Batch 4
Initial waste volume (L)	1,260	897	564	360
Total VOC constituents (L)	272	664	69	12.8
Stripping and heating time (min.)	125	103	57	50
Stripping time (min.)	86	87	57	33
Steam rate (L/min)[b]	5.9	4.69	2.82	2.64
Ratio of steam consumption to recovered VOCs	2.72	0.73	2.33	10.4
Overhead product (L)	581	1,060	225	143
Organic phase	333	660	45	3.1
Aqueous phase	248	400	180	140
Total VOC constituents[b]	271.2	662.7	64.6	12.7
Stripper residual (L)	1,420	320	545	349
Oil content	Negligible	233	Negligible	Negligible
Water content	1,420	87	539	344
VOC content	0.82	1.3	4.4	0.14
Percent VOC removed	99.7	99.8	93.7	98.7

[a] Source: Adapted from RTI. Reference No. 13.

[b] Calculated based on mass balance.

For Batch 2, stripping rate showed a negative, linear correlation between stripping time and the logorithm of waste concentration. Methyl ethyl ketone (MEK) had a stripping rate constant which was 2.7 times that of 1,1,1-trichloroethane (1,1,1-TCE), suggesting that it has an activity coefficient in the organic mixture which is significantly higher than that of the more concentrated 1,1,1-TCE. This conclusion is supported by vapor-liquid equilibrium data. A laboratory headspace analysis of the still contents showed an equilibrium vapor-liquid partition coefficient for MEK which was 2.1 times that of 1,1,1-TCE (at 25°C), while condenser vent samples taken just prior to stripping showed a ratio of 4.3 to 1 in the vapor phase.

Correlations between stripping time and the logarithm of waste concentration were also nearly linear for Batches 3 and 4, since these had a fairly high proportion of VOCs in the aqueous phase. However, stripping rate constants presented by RTI do not correlate well with aqueous phase thermodynamic property data (e.g., Henry's Law constant, vapor pressure, solubility, activity coefficient), due to the competing mass transfer mechanisms of liquid-liquid diffusion and volatilization from the organic phase. Stripping rate constants also could not be compared with relative volatility data provided by headspace analysis, since the organic phase was not fully characterized (see Table 7.3.4) and, therefore, initial constituent concentrations are unknown. Batch 2, which had a large fraction of VOCs in the organic phase, showed poor correlation between the aqueous phase concentration data (Table 7.3.4) and stripping rate constants developed by RTI.

RTI also collected air emissions data from the condenser vent and developed emissions factors based on the results. Batch 1 showed a total VOC emission factor of 5.7×10^{-5} g/g VOC recovered and Batch 2 showed a value of 2.7×10^{-5} g/g VOC recovered.

Several conclusions can be drawn from RTI's analysis:

- As recoverable solvent concentration in the waste decreases, steam consumption and cost will increase dramatically per unit of recovered solvent;
- Headspace analyses provide the most reliable estimate of relative volatility between compounds in a given waste;

- Stripping rate of a given compound in a single-phase waste shows a linear relationship between time and the logarithm of concentration. This relationship can be used to estimate stripping times required to achieve desired treatment levels. For example, RTI predicted that 40 minutes would be required to reduce 1,1,1-TCE levels in Batch 3 by an order of magnitude with the processing conditions summarized in Table 7.3.5. However, this correlation was not adequately demonstrated at low concentrations such as those specified in the solvent treatment standards;
- Use of Henry's Law constant as provided in the literature significantly overestimate the stripping rate as determined through sampling;
- Batch steam stripping of the four waste streams was not economically or technologically capable of reducing solvent concentrations to the EPA-specified treatment standards. All overhead and bottoms products required additional treatment to meet the standard. Further stripping would have resulted in overhead product which contained excessive amounts of water and, therefore, negated the beneficial effect of treatment; and
- Recovery could have been improved by indirect heating of the waste prior to steam stripping and segregation of overhead product during the course of each batch run.

Industrial Steam Stripper Survey (OSW)--

The EPA Office of Solid Waste compiled operating and cost data from 18 Supplemental 308 Questionnaires for 36 full-scale industrial steam strippers.[7] Influent and effluent solvent concentration data were collected for four steam strippers and one steam stripper/carbon adsorption combination system. Data for compounds which had influent concentrations exceeding 2 ppm are summarized in Table 7.3.6.

All waste streams shown in Table 7.3.6 were contaminated wastewaters. However, waste constituents other than priority pollutants and processing conditions were not provided in the reference. Thus, sampling results cannot be interpreted in relation to these variables.

All solvent compounds, with the exception of nitrobenzene, were stripped to levels of 2 ppm or less. Nitrobenzene was treated at two facilities (Facility Nos. 246A and 297) in wastewater streams which also contained benzene. With influent concentrations ranging from 87 to 1,966 ppm,

TABLE 7.3.6. INDUSTRIAL STEAM STRIPPER SURVEY

Plant	Compound name	Number of observations[a]	Number of nondetectable concentrations	Concentration[a]			Mean removal efficiency (minimum)
				Mean (mg/L)	Minimum (mg/L)	Maximum (mg/L)	
284	1,2-Dichloroethane	15/15	0/7	9,615/0.056	2,340/0.010	23,476/0.374	99.99+
	1,1,2-Trichloroethane	8/15	0/15	6.811/0.010	0.220/0.010	14.50/0.010	99.85
	Chloroethane	15/15	0/15	20.39/0.050	0.690/0.050	42.00/0.050	99.75
	Chloroform	15/15	0/13	399.3/0.010	7.330/0.010	1,088/0.016	99.99+
	1,1-Dichloroethene	15/15	0/14	4.358/0.010	0.200/0.010	10.80/0.013	99.77
	Trans-1,2-Dichloroethene	15/15	0/13	13.68/0.014	4.860/0.010	43.00/0.057	99.90
	Methylene chloride	5/5	0/5	5.132/0.010	2.400/0.010	12.10/0.010	99.81
	Trichloroethylene	9/9	0/7	3.049/0.019	0.210/0.010	10.30/0.085	99.38
246A	Benzene	14/13	0/6	819.9/0.045	0.239/0.010	2,008/0.171	99.99
	Nitrobenzene	15/15	0/0	391.0/251.3	91.20/94.23	1,966/619.6	35.73
225	Methylene chloride	7/7	0/4	1.973/0.308	1.290/0.010	5.100/0.985	84.39
248	Toluene[b]	1/1	0/1	8.650/0.010	8.650/0.010	8.650/0.010	99.88
297	Benzene	10/10	0/10	92.16/0.010	34.69/0.010	147.2/0.010	99.99
	Nitrobenzene	10/10	0/0	190.4/11.79	87.00/4.600	330.0/21.99	93.81

[a] Number of observations and concentration data given in the form of influent/effluent.
[b] Data includes steam stripping and carbon adsorption.

Source: U.S. EPA, Reference No. 7.

nitrobenzene was stripped to effluent concentrations ranging from 4.6 to 620 ppm. Removal efficiency at the two facilities averaged only 36 and 94 percent. In contrast, benzene was consistently stripped from similar inlet concentrations to levels below 2 ppm with removal efficiencies in excess of 99.99 percent. Benzene has a vapor pressure and Henry's Law constant which is over two orders of magnitude higher than nitrobenzene. This, combined with possible low temperature operation, account for the marked differences in removal rates achieved for these two compounds.

Industrial Steam Stripper Survey--

As part of a program to develop pollution control standards for the pesticide chemicals industry, the USEPA Effluent Guidelines Division evaluated achievable performance of full-scale steam strippers used in the industry.[14] In addition, the EPA summarized available steam stripper performance data from the organic chemicals industry which were used to strip pesticide chemical compounds. Table 7.3.7 summarizes these data for solvent compounds which were present in the influent wastewater stream at levels exceeding 2 ppm. Eight full-scale systems were identified which stripped pesticide wastes. Of these, concentration data were provided for only three units as summarized in Table 7.3.7.

Plant 1 used a steam stripper to recycle methylene chloride. The stripper operated at 960 gph feed with a nominal steam flow of 23 percent of the feed rate. The column contained 15-feet of packing using 1-inch polypropylene saddles. Removal efficiency was 99.9 percent which was sufficient to reduce the effluent concentration to less than 0.01 ppm.

Plant 2 operates a 24-tray steam stripper to remove chloroform and hexane from pesticide wastewater. A feed rate of 2,700 gph is preheated and stripped to less than 5 mg/L at a removal rate of over 93 percent. Overhead product is incinerated onsite. No breakdown between chloroform and hexane concentration was provided.

Plant 3 operates a vacuum stripper to reduce toluene levels and wastewater temperature as a pretreatment step for resin adsorption. Toluene had to be reduced to a level which would eliminate agglomeration in the resin

TABLE 7.3.7. FULL-SCALE INDUSTRIAL STRIPPER PERFORMANCE SUMMARY

Plants using steam stripping	Stripped compound	Concentration (ppm) Influent	Concentration (ppm) Effluent	Percent removal	Sampling period (days)
Pesticide industry					
Plant 1	Methylene chloride	<159	<0.01	99.9	3
Plant 2	Chloroform and hexane	70.0	<5.0	>92.6	-
Plant 3	Toluene	721	43.4	94.0	≥4
Organic chemicals industry					
Plant 4	Benzene	<15.4	<0.230	98.5	≥30
Plant 5	Methylene chloride	<3.02	<0.0141	99.5	≥40
	Toluene	178	<52.8	>70.3	
Plant 6a	Methylene chloride	1,430	<0.0153	>99.99	7
	Carbon tetrachloride	<665	<0.0549	>99.99	
	Chloroform	<8.81	1.15	<86.9	
Plant 6b	Methylene chloride	4.73	<0.0021	>99.95	7
	Chloroform	<18.6	<1.9	89.8	
	1,2-Dichloroethane	<36.2	4.36	88.0	
	Carbon tetrachloride	<9.7	<0.030	99.7	
	Benzene	24.1	<0.042	>99.8	
	Toluene	22.3	<0.091	>99.6	
Plant 7	**Methylene chloride**	34	<0.01	>99.97	1
	Chloroform	4,509	<0.01	>99.99	
	1,2-Dichloroethane	9,030	<0.01	>99.99	

Source: U.S. EPA Effluent Guidelines Division, Reference No. 14.

system regenerate. Vacuum operation reduces stream temperature, thereby improving resin adsorptivity. Thus, this stripping system was not designed to achieve maximum removal efficiency. Instead, the goal was optimal cost effectiveness when applied in conjunction with adsorptive polishing which resulted in a design stripper removal efficiency of 98.3 percent (actual removal was 94 percent).

Other industrial steam strippers used in pesticide wastewater treatment applications were identified, but not sampled. Solvent wastes treated include xylene, isobutyl alcohol, methanol, toluene, 1,2-dichloroethane, ethylene dichloride, and methylene chloride at inlet wastewater flow rates ranging from 33,000 to 90,000 GPD.

The USEPA also evaluated steam strippers used in the organic chemicals industry. Inlet and effluent solvent concentrations and removal efficiencies for five strippers are summarized in Table 7.3.7. As shown, all compounds were removed to levels below 2 ppm except for toluene (<52.8 ppm, Plant 5) and 1,2-dichloroethane (4.36 ppm, Plant 6B). As stated previously, Plant 5 is operated only as a pretreatment method which explains why toluene was not stripped to a greater extent. Converse1y, Plant 7 is operated to achieve maximum removal efficiency and was capable of achieving removal rates of 99.99 percent for all compounds.

The data which, in general, represented results of long-term testing, demonstrate the difficulty of predicting removal efficiency on the basis of single thermodynamic property correlations. For example, Henry's Law constants for methylene chloride and chloroform are nearly the same, but methylene chloride appears to be much more easily stripped (Plant 6A and 6B). Similarly, toluene has a higher Henry's Law constant than methylene chloride, but was not as easily stripped (Plant 5). This effect may be explained by the fact that methylene chloride has a higher vapor pressure than either of the other compounds. Vapor pressure may be a better indicator of attainable removal efficiency for stripping towers equipped with rectifying sections or which otherwise yield concentrated overhead products. In these instances, Henry's Law assumption of a dilute aqueous solution does not apply.

Bench-Scale Steam Strippers--

GSRI, under contract with the USEPA Office of Research and Development, performed laboratory scale investigations of steam stripping petrochemical processing wastewater streams containing biorefractory halogenated organics. Detailed analyses of individual contaminant concentrations were performed for two separate streams.[15]

The bench-scale steam stripper consisted of a 5.08 cm diameter column packed with polypropylene Pall rings to a bed depth of 367 cm. The column design was counterflow with provisions for reflux of decanted aqueous phase overhead. Overhead and bottoms product samples were composited throughout the run, whereas the feed stream analysis for individual constituents was based on a single sample collected at the end of the trial. A mass balance analysis indicated that significant quantities of VOCs were emitted from the overhead product. Thus, percent removal data were determined on the basis of bottoms and feed concentrations. Since some variability in feed composition was evident (see TOC data in Table 7.3.8), the calculated removal efficiencies may deviate somewhat from actual conditions. Additional detail on experimental design and procedures may be found in the reference.

Processing and individual compound removal efficiency data for steam stripping of stream 221A are summarized in Tables 7.3.8 and 7.3.9, respectively. The primary VOCs in stream 221A were ethylene dichloride and 1,2-dichloroethylene followed by dichloromethane, chloral and 1,1,1,2-tetrachloroethane (Table 7.3.9). No correlation between thermodynamic property data and removal efficiency was observed although chloral showed consistently low removal efficiency. This is probably a result of its high solubility and only moderate volatility which result in a low partial pressure relative to other VOCs in the waste.

In the cases with no reflux, removal of VOCs correlated positively with overhead volume, as would be expected. Addition of reflux, if anything, impaired removal efficiency due to the experimental set-up. Reflux, consisting of the decanted overhead aqueous phase, was introduced at the

TABLE 7.3.8. PROCESSING DATA FOR BENCH-SCALE STEAM STRIPPING OF STREAM 221

Test[a]	1	2	3	4	5	Volume Weighed Average
Volume (mL/min)						
Overhead (total)	5.76	7.05	12.75	13.86	13.5	10.58
Bottoms	250	281.25	302.5	305	275	282.75
Net overhead as a percentage of feed (%)	2.3	2.82	5.10	2.3	2.5	3.07
Steam (mL/min)	44.98	53.1	50.8	59.7	59.7	53.66
Ratio of reflux to net overhead	0	0	0	1.411	0.8511	0.35
Stripper column TOC (mg/L)						
Bottoms	256	292	293	241	243	265.3
Overhead	10,446	10,462	4,766	4,519	9,806	7,516
Feed	645	668	645	785	636	675.8
Total TOC removal (%)	60.3	50.8	45.0	62.5	58.0	60.7
Stripper column VOC (mg/L)						
Bottoms	809	651	507	853	1,111	734
Overhead	11,639	11,850	11,240	9,621	16,297	12,010
Feed	-	-	-	-	-	5,480
Total VOC removal (%)	85.2	86.6	88.8	81.0	77.7	84.3
Selected VOC removal (%)[b]	86.7	87.3	90.8	81.4	78.0	-

[a] Processing conditions: column feed = 250 mL/min for all tests. Pressure = 1 atm, temperature of overhead and bottoms ranged from 102 to 104°C.

[b] This data includes only those VOCs which were quantified for all five test runs to permit comparison between different processing conditions.

Source: Adapted from GSRI, Reference No. 15.

TABLE 7.3.9. SUMMARY OF REMOVAL EFFICIENCY DATA FOR STREAM 221A

Compound	Feed composition (mg/L)	Removal efficiency[a]		
		Minimum	Maximum	Average
Vinylidene chloride	61.5	46.7	100	82.2
Dichloromethane	800.9	54.9	87.4	76.7
1,2-Dichloroethylene	1,583.3	76.4	100	85.9
Chloroform	140.3	49.3	100	89.9
1,1,1-Trichloroethane[b]	50.9	10.1	10.1	10.1
Ethylene dichloride	1,593.0	69.9	97.4	91.3
Trichloroethylene	0	NA	100	NA
Chloral	693.2	18.3	75.2	53.1
1,1,2-Trichloroethane	14.1	98.7	100	99.8
Perchloroethylene	14.9	54.3	100	77.2
1,1,1,2-Tetrachloroethane	512.8	99.7	100	99.9
1,1,2,2-Tetrachloroethane	14.9	NA	100	NA

[a] Based on bottoms and feed concentration and flow data.
[b] Only one sampling data point available.

Source: Adapted from GSRI, Reference No. 15.

column midpoint, whereas waste feed was introduced at the top of the column. Thus, the overhead product composition is essentially limited by the equilibrium vapor concentration of the feed and, therefore, independent of reflux. However, if the reflux was more concentrated in VOCs than the wastewater at the column midpoint, removal efficiency would decrease with addition of reflux, particularly for water soluble compounds which would be preferentially returned to the column.

In summary, recovery of VOCs averaged 85 percent with steam flows of 18 to 24 percent of the feed. Recovery was limited due to column design as indicated by the insensitivity of recovery rates to steam consumption and reflux. With the exception of chloral (low removal efficiency), the relative removal efficiencies of different compounds could not be differentiated due to uncertainties in the feed composition and fugitive emissions.

GSRI also performed sampling on a second waste (Stream 11C) which was from an oxyclor operation manufacturing ethylene dichloride. The VOCs (1,999 mg/L) consisted almost entirely of ethylene dichloride (95.7 percent). Table 7.3.10 summarizes flow rates and ethylene dichloride concentrations for feed, overhead, and bottoms streams along with steam and reflux flow measurements. Only runs for which all data were collected were included in Table 7.3.10.

Overall material balances for this trial were good, but VOC losses from the overhead product occurred. As a result, removal efficiencies presented in Table 7.3.10 are based on bottoms and feed composition and flow data. Removal efficiency correlated positively with overhead to feed ratio (i.e., increased steam as a percentage of feed rate) and negatively with increased feed rate (i.e., lower contact time). An overhead to feed ratio of 5 to 6 percent (steam to feed ratio of 21.5 percent) or more was necessary to achieve greater than 99 percent removal efficiency at feed rates up to 400 mL/min. Further increases in steam or reflux showed little improvement suggesting that equilibrium and mass transfer limitations restricted further volatile removal.

TABLE 7.3.10. SUMMARY OF PROCESSING DATA FOR BENCH-SCALE STEAM STRIPPING OF ETHYLENE DICHLORIDE

Run Nos.	Flow rates (mL/min)					Ethylene dichloride (mg/L)			Removal efficiency	Steam/Feed ratio (%)
	Feed	Overhead	Bottoms	Reflux	Steam	Feed	Overhead	Bottoms		
1	395	11.4	410	0	69	1,716	8,835	65	96.1	17.5
12	245	55.0	290	0	87	10,734	16,278	0.3	99.9+	35.5
28	390	21.7	460	0	84	5,640	19,629	43	99.1	21.5
31	260	15.7	300	0	56	5,189	16,409	3.7	99.9+	21.5
32	290	9.1	350	0	65	5,762	18,100	5.7	99.9	22.4
36	350	18.3	400	0	80	1,463	6,587	6.0	99.5	22.9
37	225	12.0	279	0	55	1,247	6,838	9.2	99.1	24.4
39	240	14.1	309	0	56	1,426	6,030	7.0	99.4	23.3
41	250	42.3	285	33.3	77	1,457	4,925	6.1	99.5	30.8

Source: Adapted from GSRI, Reference No. 15.

Except for a single optimal operating condition (Run No. 12; low feed rate, high steam addition), a residual solvent concentration below 2 ppm was not achieved. However, with high steam flow and addition of a rectifying section, it is likely that this level could be reached while still maintaining a low volume, separable overhead product.

Other parameters recorded during the trials include: ethylene dichloride range of 1,247 to 10,734 mg/L in the feed stream with 96.1 to 99.9+ percent removal; chemical oxygen demand reduction of 66.5 percent from 464 mg/L; total organic carbon reduced by 83.4 percent from 790 mg/L; and total oxygen demand reduced by 95.7 percent from 5,190 mg/L.

Bench-Scale Ground Water Stripping Feasibility Study--

Several wastewater treatment technologies, including steam and air stripping, were evaluated in bench-scale treatability studies to select the best combination of unit processes to treat contaminated ground water. A continuous-flow packed column was used for the testing with air and steam flowing countercurrent to the ground water. The column was 3-1/8 inches in diameter and 48 inches long with 26 inches of packing using 7 mm glass Raschig rings.[16]

Test conditions and TOC removals for the steam stripping study are given in Table 7.3.11. Runs were performed with and without lime pretreatment and activated carbon post-treatment, as noted in the table. The stripping removal rates for specific volatile and extractable organics are detailed in Table 7.3.12. All volatile organics were present in the raw water above 2 ppm and were included in the analysis.

At steam to feed ratios ranging from 31 to 56 percent by weight and air to feed ratios of 6 to 56 percent (i.e., Runs 1 through 5), total VOC removal efficiency consistently exceeded 99 percent. On average, total VOCs in these runs were reduced by 99.87 percent from 771 to 1 mg/L. The lowest removal rate reported for an individual compound was 98.6 percent for 1,1,1-trichloroethane in Run 4. Extractable organics were reduced by 94 percent from 2.6 to 0.2 mg/L. The data in Table 7.3.11 suggest that removal of organics was essentially complete at these experimental conditions (Runs 1 through 5) since removal rate showed little response to increased air, steam, or wastewater flow rate.

TABLE 7.3.11. TEST CONDITIONS AND TOC REMOVALS FOR BENCH-SCALE STEAM STRIPPING WITH/WITHOUT ACTIVATED CARBON

	Water flow (L/min)		Air flow		Final temperature (°C)		TOC (mg/L)[b]	
Sample[a]	Before steam	After steam	L/s	cfm	Water	Air	Air and steam stripping	Steam stripping plus activated carbon[c]
Run 1	0.13	0.17	0.11	0.25	85	35	1,500	-
Run 2	0.13	0.17	0.11	0.25	86	35	1,700	870
Run 3	0.045	0.07	0.11	0.25	83	83	900	400
Run 4	0.045	0.07	0.23	0.50	79	79	900	500
Run 5	0.045	0.07	0.35	0.75	74	73	800	400
Run 6	0.08	0.095	0.47	1.0	69	42	1,615	-
Run 7	0.35	0.37	0.47	1.0	46	22	3,633	-

[a] Initial TOC concentration was 4,000 mg/L.

Test conditions for Run 1-5:
air temperature = 24°C
water temperature = 23°C
pH = 6.0

Test conditions for Run 6 & 7:
air temperature = 22°C
water temperature = 22°C
pH = 6.0

Raw sample was treated with lime to pH 20.0 for metals removal; then the pH was adjusted to 6.5 with sulfuric acid.

[b] The TOC measurement is for diluted effluent (increased flow due to condensate).

[c] 50,000 mg carbon/liter. Use of activated carbon alone reduced TOC to 2,240 mg/L.

Source: Adapted from Reference No. 16.

TABLE 7.3.12. RESULTS OF BENCH-SCALE STEAM STRIPPING RUNS PERFORMED WITH/WITHOUT LIME PRETREATMENT

Compound	Concentrations in ground water (no pretreatment) - ug/L						Concentration for ground water with lime pretreatment - ug/L			
	Raw water	Run 1	Run 2	Run 3	Run 4	Run 5	Feed to Stripper	Stripper effluent	Run 6	Run 7
Volatile organic compounds										
Tetrahydrofuran	22,000	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
1,1,1-Trichloroethane	150,000	[a]	[a]	150	2,135	[a]	123,000	123,000	2,830	23,60
Benzene	68,750	[a]	[a]	290[b]	1,640[b]	[a]	51,000	18,250	25	113,00
Trichloroethylene	338,000	[a]	[a]			[a]	330,000	100,000	213	
Methyl isobutyl ketone	76,400	[a]	[a]	[a]	[a]	[a]	78,000	58,600	1,300	38,90
Xylene	[a]	[a]	[a]	[a]	[a]	[a]	517	80	[a]	8
Toluene	92,000	126	[a]	[a]	[a]	53	98,400	51,600	975	30,60
Ethylbenzene	23,500	[a]	[a]	[a]	992	[a]	1,636	1,636	[a]	1,63
Extractable organic compounds										
1,4-Dichlorobenzene	35	-	17	-	-	-	930	930	[a]	20
1,2-Dichlorobenzene	5	-	[a]	-	-	-	260	260	≤1	[illegible]
Naphthalene	51	-	≤1	-	-	-	9	9	≤1	2
2-Chlorophenol	540	-	40	-	-	-	75	75	[a]	-
2-Nitrophenol	15	-	6	-	-	-	150	150	150	-
Phenol	370	-	20	-	-	-	70	70	40	-
2,4-Dimethylphenol	20	-	[a]	-	-	-	80	80	80	-
o-Cresol	80	-	25	-	-	-	200	200	200	-
m-Cresol	220	-	[a]	-	-	-	[a]	[a]	[a]	-
Benzoic acid	1,230	-	[a]	-	-	-	90	90	70	-
Pentachlorophenol	40	-	40	-	-	-	40	40	2	-

[a] None detected (no peaks on chromatograms).

[b] Benzene and trichloroethylene peaks combined into one peak.

Source: Adapted from Reference No. 16.

During these steam stripping runs the packing materials became heavily coated with oxidized iron and manganese. It was decided to treat the raw water with lime to increase the pH to 10.0 to precipitate heavy metals. The pH was then adjusted to 6.5 with sulfuric acid prior to steam stripping. Lime treatment was effective in reducing fouling of the packing by reducing metal concentration in the feed from 442 mg/L to less than 2 ppm. However, lime treatment did not significantly reduce the concentrations of volatile organics as shown in Table 7.3.12.

Runs 6 and 7 were performed with pretreated wastewater at steam-to-feed ratios of 19 and 6 percent and air-to-feed ratios of 42 to 10 percent by weight, respectively. Total VOC removal efficiency was 98.5 percent for Run 6 and only 41.2 percent for Run 7.

Comparison of these results with those obtained for Runs 1 through 5 suggest that steam stripping is significantly more effective than air stripping when equal quantities of stripping agent are applied. Furthermore, stripping efficiency is enhanced as the ratio of stripping medium to feed and contact time increase, as expected.

The last phase of the steam stripping study involved evaluating the effectiveness of activated carbon adsorption in treating atmospheric emissions from the stripper. During Run 6, portions of the off-gas were pulled through an activated carbon bed and the adsorbed volatile organics were analyzed by gas chromatograph purge-and-trap procedures. The results, which clearly indicate the effectiveness of this treatment method, are summarized in Table 7.3.13. The volatile organic load applied to the carbon and the corresponding amount of volatile organics removed per weight of carbon are shown. VOC removal ranged from 100 percent at a carbon loading of 1.9 μg/mg to 95 percent at 5.7 μg/mg loading.

7.3.3 Cost of Steam Stripping

Steam stripping costs are highly site specific. Large-scale units used for stripping wastewater streams are custom designed for specific applications. As a result, equipment manufacturers are reluctant to supply cost estimates without detailed waste characteristic and volume data for specific applications.

TABLE 7.3.13. TEST RESULTS FROM CARBON ADSORPTION OF OFF-GAS FROM STEAM STRIPPING - RUN 6

Volatile organic compound	Volatile organic stripped µg/min	Volatile organic loading applied to carbon[a] µg/mg	Volatile organic adsorbed µg/mg
1,1,1-Trichloroethane	9,570	0.8	0.8
	9,570	1.6	1.6
	9,570	2.4	2.2
Benzene	1,457	0.07	0.07
	1,457	0.21	0.20
Trichloroethylene	7,980	0.13	0.13
	7,980	0.40	0.37
Methyl isobutyl ketone	4,564	0.52	0.52
	4,564	1.05	1.05
	4,564	1.57	1.51
Toluene	4,035	0.31	0.31
	4,035	0.62	0.62
	4,035	0.94	0.94
Ethylbenzene	131	0.06	0.06
	131	0.13	0.13
	131	0.17	0.17
Total volatile organics	27,737	1.89	1.89
	27,737	5.69	5.39

[a] Carbon used was GAC-40; Carborundum, Niagra Falls, N.Y.

Source: Reference No. 16.

Cost of these units is basically a function of throughput, initial VOC concentration and relative volatility of the compounds which are to be stripped. Flow rate determines the diameter of the column (without reflux), initial concentration determines the required removal efficiency to meet effluent treatment standards, and relative volatility determines the ease with which VOCs can be stripped. Depending on relative volatility, a tradeoff between column height, reflux, steam rate, operating pressure, and post-treatment costs can be established.

Treatment cost data presented in the literature were generally not useful for predicting total waste treatment costs for a range in waste characteristics. RTI[13] presented cost data for the four batches of solvent waste discussed in Section 7.3.4. However, these data were for specific wastes treated in an offsite facility and, therefore, were not indicative of general onsite processing costs. Water General[9] presented a detailed design and treatment cost modeling approach. However, this methodology does not include an evaluation of post-treatment costs or cost reductions achieved through solvent recovery. For dilute wastewaters, these costs can effectively be ignored since they are relatively small and offset one another. However, these costs can represent significant fractions of total waste processing costs for more concentrated wastes, and therefore must be taken into consideration.

Two cost analyses are presented below. The first provides capital and operating cost equations for steam stripping of dilute wastewater streams. It is based on a review of actual onsite steam stripping installations performed by JRB Associates.[8] The second analysis, performed by GCA, is appropriate for developing cost estimates for more concentrated solvent wastes. This analysis takes into consideration three residual disposal options (wastewater treatment, use as a fuel, incineration) and discusses the impact of various waste characteristics and cost centers on overall processing costs.

Steam Stripping Costs for Wastewater Streams--

JRB analyzed cost and design data for 15 industrial steam strippers used to recover secondary materials or organic priority pollutants from wastewaters that flowed into secondary biological treatment systems.[8] Steam strippers used to recover or recycle primary products/raw materials were excluded from this analysis since they differ in design from units used to treat wastewater. In addition, tray towers were chosen for use in the analysis instead of packed towers since data on these units were more readily available.

Capital and operation and maintenance (O&M) costs were normalized to 1980 dollars using the appropriate Engineering News Record indices. Where installation costs were not provided, they were assumed to be 50 percent of capital costs. Capital costs include: stripping columns, feed tanks, feed preheaters, condensers, decanters, organic phase pumps, bottom pumps, and existing equipment modifications. O&M costs include: operation and maintenance labor, maintenance materials, steam, and electricity.

An analysis was performed to determine a mathematical relationship between capital and O&M costs and significant steam stripper design parameters such as contaminant volatility, wastewater flows, column diameter, and column height. The results of this analysis showed that capital costs were best related to the diameter (D, in inches) and height (H, in feet) of the column, while O&M costs were best related to the diameter and wastewater flow (Q, in million gallons/day) as follows:

$$\text{Capital cost (in million dollars)} = 0.246 - 2.88 \times 10^{-4} (D) + 1.546 \times 10^{-6} (D^2 H)$$

$$\text{O\&M cost (in million dollars)} = 3.68 \times 10^{-3} (D) + 0.809 (Q) - 0.023$$

Overall, predicted capital costs were within a factor of 3 of reported costs, O&M cost estimates were within a factor of 5, and cost per gallon of treated waste was within a factor of 3.7 of actual values. With an annual capital recovery factor of 0.177, capital costs accounted for an average of 26 percent of total cost per gallon of treated waste. Excluding a single facility which had a low capacity utilization (largest diameter tower but lowest flow rate), cost per gallon of treated waste averaged 0.9 cents per gallon with a range of 0.14 to 20.4 cents per gallon. Costs for four packed towers, excluded from the analysis, averaged 1.12 cents per gallon. Since flow rates to these units were only one-fourth of that in the average tray column, the cost difference may be attributable to economies of scale.

The above data are applicable to steam stripping costs for continuous flow columns treating dilute (i.e., less than 1 percent solvent) organic contaminated aqueous wastes. They do not include waste pretreatment and bottoms post-treatment costs or net cost benefits derived from solvent recovery. Overhead products will consist of a solvent-water mixture which will require further treatment (e.g., distillation, additional stripping) to recover a valuable product. This additional processing is likely to result in a small net cost advantage relative to raw material purchasing, and thus its effect can be ignored. Bottoms post-treatment will be required if solvent concentrations continue to exceed disposal limitations or if the waste is still considered to be hazardous due to the presence of other nonvolatile contaminants. Post-treatment by activated carbon, biological treatment, or other methods will add roughly 2 cents per gallon to waste treatment costs.

JRB also attempted to determine cost variability as a function of contaminant volatility. JRB used the design methodology provided by Water General Corporation[9] to determine variability in column height and therefore, capital cost, which is required to strip compounds with different Henry's Law constants. Water General's methodology involves calculation of a stripping factor which is proportional to Henry's Law constant, the vapor/liquid flow ratio, and the reciprocal of tower operating pressure.

JRB assumed a steam-to-liquid feed ratio of 10 percent and atmospheric column operating pressure. Costs were based on stripping to a maximum residual VOC concentration of 1 ppm. Minimum column diameter was set at 1.0-feet and minimum height at 10 feet to reflect wastewater processing equipment currently in use.

Table 7.3.14 summarizes the resulting cost data based on the above assumptions. As shown, cost per gallon of waste treated shows little variability between compounds with different volatility. However, if JRB's column size constraints were removed, the data would show lower treatment costs for wastes with highly volatile constituents and low flow rates. Also, operating costs would constitute a higher fraction of total costs since optimal operating conditions would, in some cases, be represented by higher steam rates instead of increases in column height.

TABLE 7.3.14. STEAM STRIPPING COSTS FOR WASTEWATER STREAMS CONTAINING CONTAMINANTS OF VARYING HENRY'S LAW CONSTANT

Henry's Law constant range	Example compound	Flow Rate (MGD)	Height (ft)	Diameter (ft)	Capitol Cost ($MM)	O&M Cost ($MM)	Unit cost (¢/gal)[a]
Greater than 10^{-1}	1,1,1-Trichloroethane	1.0	10.0	6.28	0.312	1.06	0.36
		0.10	10.0	2.11	0.249	0.151	0.63
		0.01	19.6	1.00	0.247	0.029	2.30
10^{-2} to 10^{-3}	Acrylonitrile	1.0	14.2	6.28	0.349	1.06	0.36
		0.10	18.8	2.11	0.257	0.151	0.63
		0.01	30.9	1.00	0.249	0.029	2.30
Less than 10^{-4}	Nitrobenzene	1.0	36.1	6.28	0.540	1.06	0.37
		0.10	42.9	2.11	0.281	0.151	0.64
		0.01	65.2	1.00	0.257	0.029	2.40

[a] Assuming 312 operating days/year and an annual capital recovery factor of 0.177.

Source: Adapted from JRB. Reference No. 8.

Steam Stripping Costs for Nonaqueous Wastes--

GCA performed a cost analysis for steam stripping of nonaqueous wastes using three nominal flow rates (10, 50, and 500 gpm) and three disposal methods (wastewater treatment, use as a fuel, incineration). The cost of stripping concentrated wastes (i.e., greater than 1 percent solvent) is highly dependent on method of disposal. Other major cost variables considered included capital, installation, maintenance, labor, overhead and utility costs and value of recovered solvent.

Capital costs for process equipment, tanks, engineering, electrical and instrumentation were taken from the literature.[17] A contingency of 15 percent and an annualized cost of 17.7 percent of the total were assumed as summarized in Table 7.3.15. Maintenance costs for stream strippers were based on an EPA estimate of 4.13 percent of annualized capital cost.[9] Labor costs were assumed to be $14.42/hour including overhead.[17] Labor usage was assumed to range linerly from 0.5 to 3.0 operators for the flow rates under consideration with a base case operating time of 2,080 hours/year.

Utility costs were assumed to average $0.04/gallon of recovered solvent. This value is based on the cost of steam ($3.00/million Btu)[9], electricity ($0.04/KWH)[17], and cooling water ($0.25/1,000 gallons)[17] which is necessary to separate and condense solvents from a solvent-water mixture. This value will vary depending on the solvent which is to be recovered. For example, at 1 percent solvent concentration, utility costs will range from approximately 2 cents (e.g., acetone) to 7 cents (e.g., nitrobenzene) per gallon of recovered solvent, depending primarily on the solvent boiling point in the mixture. Utility costs for concentrated solvent waste depend on both the boiling temperature and heat of vaporization of the solvent, and range from roughly 3 to 6 cents per gallon of recovered solvent.[17] However, since utility costs generally represent a small fraction of total treatment costs, an average value of 4 cents per gallon was assumed.

Three methods of bottoms disposal were used in this analysis. Wastewater treatment technologies such as adsorption and biological treatment were assumed to cost 2 cents per gallon. Organic bottoms which could be used as a fuel substitute were assumed to cost $0.20/gallon and bottoms which required incineration (e.g., liquid injection) were assumed to cost $2.00/gallon.

TABLE 7.3.15. COST COMPONENTS FOR ONSITE STEAM STRIPPING SOLVENT RECOVERY: (EXAMPLE CASE WITH 30% SOLVENT CONTENT AND BOTTOMS USED AS FUEL)

Nominal feed rate (gpm)	10	50	500
Capital costs			
Process equipment	8,000	39,000	72,000
Tanks	18,500	18,500	74,000
Subtotal (1)	26,500	57,500	146,000
Engineering, electrical, instrumentation (20% of (1))	5,300	11,500	29,200
Subtotal (2)	31,800	69,000	175,200
Contingency (15% of (2))	4,800	10,400	26,300
Subtotal (3)	36,600	79,400	201,500
Annualized capital cost (17.7% of Subtotal (3))	6,478	14,054	35,666
Operating and maintenance costs[a]			
Maintenance (4.13% of annualized capital cost)	268	580	1,473
Labor ($30,000/man-year including overhead)	15,000	22,800	90,000
Utility costs (4¢/gallon of recovered solvent)	237	1,186	11,856
Solvent recovery benefit cost ($2/gallon of recovered solvent)	(11,850)	(59,300)	(592,800)
Disposal cost ($0.20/gallon)	3,391	16,953	169,530
Net O&M cost	7,046	(17,781)	(319,941)
Total capital and O&M cost	13,524	(3,727)	(284,275)
Cost/gallon of waste treated	0.65	(0.04)	(0.27)
Threshold cost of recovered solvent ($/gallon)	4.24	1.83	1.00

[a] Numbers in parenthesis represent revenues.

Finally, recovered solvent was assumed to have a value of $2.00/gallon for the purposes of calculating overall unit cost of waste treated. Although many solvents have higher purchase prices, this value was used since many recovered materials will be in the form of less valuable mixtures or require additional treatment thereby increasing treatment costs.

Table 7.3.15 provides an example cost analysis for treating an organic waste containing 30 percent solvent and using the residual bottoms product as a fuel. Table 7.3.16 summarizes the results of the cost analysis for wastes ranging from 1 to 70 percent solvent for the three bottoms disposal scenarios. Cost figures are presented on the basis of cost per gallon of waste treated and threshold cost per gallon of solvent recovered.

As shown in Table 7.3.16, costs increase dramatically with increasing bottoms disposal cost, particularly for high flow rate units. For example, at 10 gpm and 10 percent solvent content, disposal costs for wastewater treatment account for only 4 percent of total treatment costs. This fraction jumps to 16 and 66 percent for use as a fuel and incineration, respectively. At a feed rate of 500 gpm, disposal costs became even more significant accounting for 24, 61, and 93 percent of total costs as more expensive disposal methods are used. Although these costs are lower for wastes with higher percentages of recoverable solvent, disposal costs will remain a significant cost component for high-volume units with nonaqueous bottoms products.

Similarly, as capacity and percent recoverable solvent increase, total treatment cost becomes increasingly sensitive to the value of recovered solvent. For example, at 10 gpm with 10 percent solvent content in the waste, total value of recovered solvent is 16 percent of processing costs (assuming $2.00 value per gallon of recovered solvent and bottoms used as fuel). This percentage jumps to 113 percent as solvent content in the feed increases to 70 percent, and increases further to 554 percent of processing costs when capacity is increased to 500 gpm. Thus, unit value of recovered solvent has an increasingly significant impact on processing economics as throughput and percent recoverable solvent increase.

Utility costs show a similar relationship to throughput and recoverable solvent content. For wastes with less than 10 percent solvent content, utility costs are only a few percent or less of total costs. However, at high

TABLE 7.3.16. STEAM STRIPPING COST ESTIMATES AS A FUNCTION OF THROUGHPUT, SOLVENT CONTENT AND DISPOSAL METHOD

Bottoms disposal method	Solvent content in waste (%)	Cost ($)/gal of waste treated[a]			Cost ($)/gal of solvent recovered[a]		
		10 GPM	50 GPM	500 GPM	10 GPM	50 GPM	500 GPM
Wastewater treatment	1	1.05	0.36	0.12	108.00	38.58	14.59
	5	0.98	0.29	0.06	21.79	7.95	3.15
	10	0.89	0.21	(0.03)	11.01	4.08	1.68
Use as fuel	10	1.05	0.37	0.13	13.11	5.90	3.39
	30	0.65	(0.04)	(0.27)	4.24	1.83	1.00
	50	0.24	(0.45)	(0.68)	2.46	1.02	0.52
	70	(0.17)	(0.85)	(1.09)	1.70	0.67	0.31
Incineration	10	2.00[b]	2.00[b]	1.93	[b]	[b]	22.36
	30	2.00[b]	1.43	1.19	[b]	6.98	6.15
	50	1.36	0.68	0.44	4.83	3.39	2.89
	70	0.61	(0.07)	(0.31)	2.88	1.85	1.49

[a] Numbers in parenthesis represent revenues.

[b] Cost of treatment via steam stripping exceeds incineration cost of raw waste ($2.00/gallon), therefore, incineration represents the lower cost alternative.

flow rate and high solvent content, these costs become significant. For example, at 500 gpm and 70 percent solvent in the feed, utilities account for 11 percent of total processing costs when bottoms are used as fuel (2.6 percent when bottoms are incinerated).

In contrast to disposal and utility costs, capital and labor represent the primary costs of processing low volume, dilute wastes. Capacity utilization is more critical for low volume units since capital costs are distributed over the total volume of waste processed. For example, increasing processing time from 8 to 16 hours per day reduces processing costs by 16 cents per gallon for 10 gpm units versus only 1 cent per gallon for 500 gpm strippers.

7.3.4 Overall Status of Process

7.3.4.1 Availability--

Steam stripping is a commonly applied waste treatment technology for the separation of low solubility solvents from water or low volatility organics (e.g., oil). The EPA has identified 27 industrial steam stripping wastewater treatment units, 11 units used by the pesticides industry, and 8 steam strippers (packed towers) used by a pharmaceutical manufacturer.[b] GCA's analysis of the commercial solvent recycling industry showed 25 percent of the reclaimers using steam distillation (Table 4.1.1).

7.3.4.2 Application--

Steam stripping is commonly used as a pretreatment method, particularly when applied to concentrated solvent wastes. Although in many cases it can be used to reduce solvent concentrations to levels which permit direct discharge, it is often more cost-effective to use other treatment methods for final bottoms processing. Steam stripping of wastewater streams is typically followed by biological treatment or adsorption systems for final effluent polishing. Stripped organic waste bottoms can be decanted and used as fuel provided that chlorine content has been sufficiently reduced in the stripper.

7.3.4.3 Environmental Impact--

Post-treatment of both the overhead and bottoms streams is usually required, although in certain instances the solvent concentration in the bottoms stream may be below proposed standards. Overhead products undergo liquid-liquid separation, typically through decanting. However, the organic solvent may require drying and the aqueous phase may require further treatment to remove dissolved organics. Air emissions from the column vent can be significant,[13] and should, at least, be monitored.

7.3.4.4 Advantages and Limitations--

Steam stripping is preferrable to other physical separation technologies in the following instances:

- For treating wastes which contain high solids or polymerizable materials which would otherwise foul heat transfer surfaces;
- For treating wastes which contain constituents that form low boiling azeotropes with water, particularly those which require low processing temperatures due to thermal degradation; and
- For treating wastes to low residual solvent content, particularly when the bottoms product would be rendered unpumpable in the absence of water.

Steam stripping is not well suited to treating wastes in which either the overhead or bottoms are difficult to separate from water. Thus, it is better utilized for separating solvents which decant readily and have low solubilities in water (e.g., halogenated organics) and less applicable to treating water soluble wastes; e.g., alcohols.

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7.4 AIR STRIPPING

7.4.1 Process Description

Air stripping is one of several processes available that effectively removes certain volatile organic compounds (VOCs) from aqueous media. Air stripping operations employ gas-liquid contacting systems to enhance the transfer of VOCs from the liquid phase to the gas phase. Various types of aeration devices have been designed to optimize transfer and they fall into two general categories: (1) injection of water into air, and (2) injection of air into water. In both systems, mechanical energy creates air-water interfaces across which mass transfer of the contaminant can occur. Examples of water-into-air systems are spray systems into the open air, spray towers, and tray and packed towers. Air-into-water systems typically used are diffused or mechanical aeration.

Each of these units has certain process and economic advantages. However, tray and packed tower aeration will be the focus of this study since they are commonly used and design criteria for tray and packed towers are available to meet desired contaminant removal efficiencies.[1] Other systems have less structured design requirements and are used primarily to supply oxygen for aerobic biotreatments.

Diffused Aeration--In a diffused aeration system, air is injected into the water through a sparging device or through porous diffusers which produce a multitude of fine bubbles. As the bubbles rise, mass transfer occurs across the water-air interface until the bubble either leaves the water column or becomes saturated with the contaminant. The rate of mass transfer and its extent can be enhanced by increasing the depth of the tank, improving bubble dispersion, decreasing the bubble size, and increasing the volumetric air to water ratio. Increasing the depth of the tank may not increase the mass transfer if the air bubble reaches saturation before it exits the liquid surface.

Generally, diffused aeration systems are operated as continuously stirred tank reactors, and are thus inherently less efficient that a counter-flow process. The system is widely used for gas adsorption, principally adsorption of oxygen for biological oxidation. Diffused aeration can also be used for removing highly volatile compounds and is the basis of the widely used purge-and-trap analytical method for concentrating organic compounds. In water treatment applications, removal of up to 90 percent has been reported for several VOCs. Removal of VOCs during aeration of activated sludge process has also been reported.

Mechanical Aeration--Air can also be introduced into water by mechanical mixing. In this system the contents of the tank or impoundment are circulated providing continuous contact between the atmospheric air and water. Principal design parameters include mixing intensity, the type of mixer, the depth of the tank or impoundment, and the residence time if the system is continuous. The system exhibits relatively low rates of mass transfer, but has the advantage of mechanical simplicity and negligible liquid head loss. The system has been used for removal of ammonia and VOCs with moderate success, but is normally used to supply oxygen for biological activity.

Sprays and Spray Towers--High rates of mass transfer can be achieved by pumping water through spray nozzles that break the liquid stream into fine droplets. Sprays can be used to inject water into the open air or into a tower. Principal design parameters for sprays and spray towers include selection of the type of nozzle, nozzle size, allowable nozzle pressure drop, and the process configuration. Because of back mixing in the tower and in the air, true countercurrent transfer does not occur and mass transfer rates are usually modest. As a consequence, removal efficiencies greater than 90 percent may not be economically feasible.

Tray and Packed Towers--The design principles for air stripping in packed and tray towers have been extensively examined in the chemical engineering literature over the past 30 to 40 years.[1] Most chemical engineering applications generally involve design of systems to treat concentrated solutions. However, the general design procedures developed in the chemical processing industry have recently been extended to cover the full range of concentrations, including the case of dilute solutions typically encountered in water treatment applications.

Tray or packed tower air stripping systems similar to those depicted in Figure 7.4.1. are more effective for the removal of organics from water than the other systems described above. The stripping medium, air, is introduced near the base of the tower, while the liquid feed is introduced near the top. As the air rises and comes into contact with the falling water, the volatile components are transferred from the organic rich water to the air. The organic laden air is carried out the top as overhead, and the stripped water exits the bottom of the tower.

In tray towers, the tower is filled with regularly spaced trays or plates allowing for staged contact between the two phases. The vapor passes through openings in each tray and contacts the liquid flowing across the tray. A quantity of liquid is retained on each tray by a weir. To reach the next stage, the liquid flows over the weir through a downcomer which provides sufficient volume and enough residence time for the liquid to be freed of entrained vapor before entering the next tray. The overall effect is a multiple countercurrent contact of air and water, although each tray is characterized by a crossflow of the two. Each tray of the tower is considered a stage.

Packed towers are simple when compared with tray towers. A typical tower consists of a cylindrical shell containing a support tray for the packing material and a liquid distributor designed to provide effective irrigation of the packing. The water is distributed over, and flows down through, the packed bed, exposing a large surface area for transfer into the air which enters at the bottom of the tower. Commercially available packing materials come in a variety of shapes and sizes. Most packings are made of either ceramic, metal, or plastic. Depending on the types and size of packing they may be either randomly dumped or carefully stacked in the column.

7.4.1.1 Pretreatment Requirements--

Pretreatment requirements for air stripping operations are usually minimal and basically related to contact equipment limitations for solids. Solid removal by filtration, sedimentation, or other means may be required to avoid plugging of spray nozzles and fouling of packing and tray towers. A limiting suspended solids content of 2 percent is called out in Reference 2.

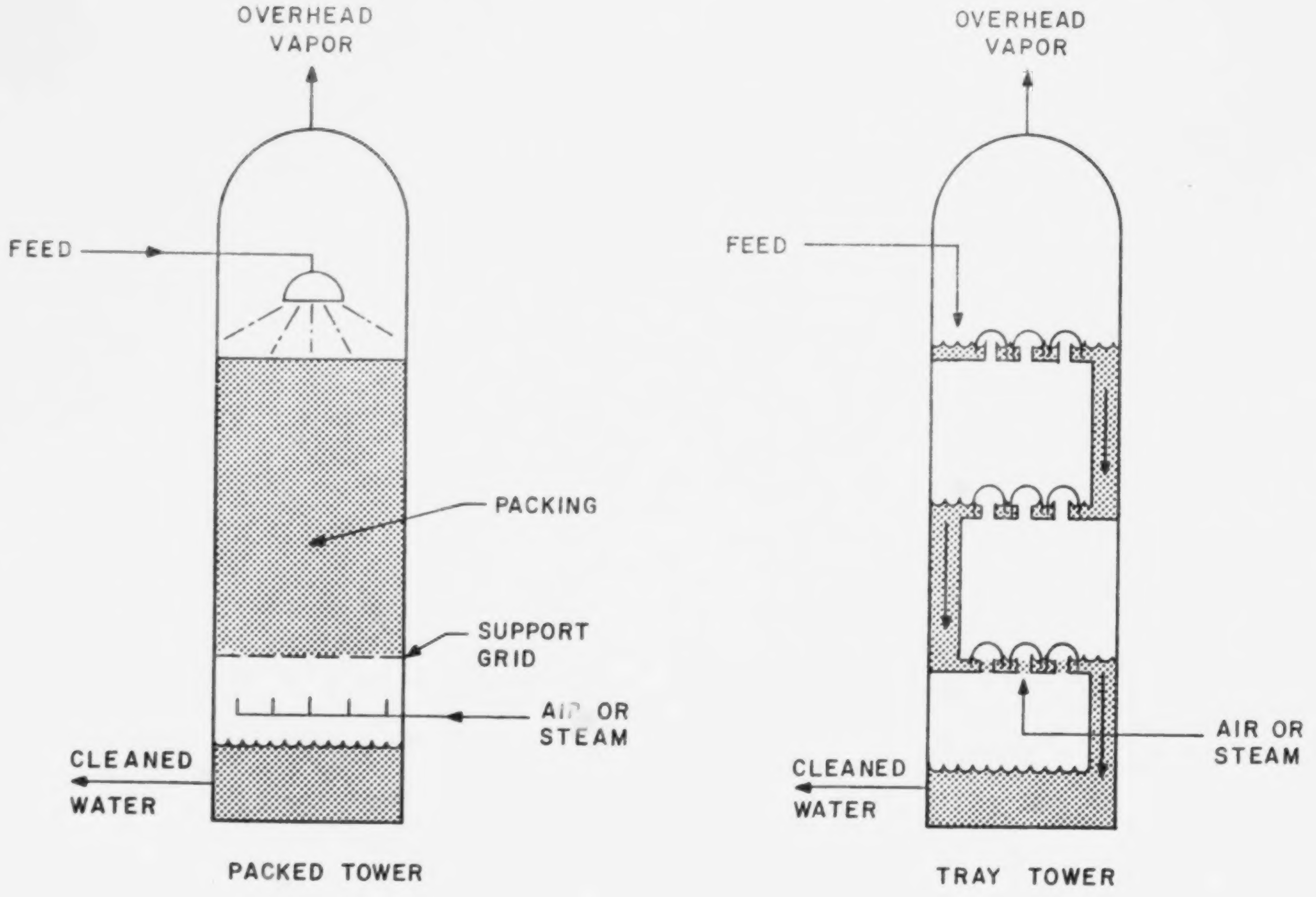

Figure 7.4.1. Air stripping towers.

The removal of oil and grease and dissolved metals which may oxidize and precipitate could also be necessary to avoid column plugging. A schematic of an air stripping system, with a variety of pretreatment and post-treatment options, is shown in Figure 7.4.2.

7.4.1.2 Operating Parameters--

Organic contaminants found in water and wastewater exhibit a wide range of water solubilities and polarities. Each compound has a different tendency to pass from the aqueous phase into the air. For aqueous mixtures containing low concentrations of VOC, the distribution of a VOC between air and water under equilibrium conditions can often be expressed by Henry's Law. It states that at equilibrium the partial pressure of a contaminant (y) in air is proportional to its concentration in water as shown below.

$$P_y = H_y X_y$$

where: P_y = Partial pressure of compound y (atm)

H_y = Henry's Law constant (atm-m^3/mole)

X_y = Molar concentration (mole/m^3)

Henry's Law is valid for mole fractions less than 10^{-3}, although the exact limit of this law depends upon the molecular interactions of the compounds in water. In general, the larger the Henry's Law constant the more easily a compound can be stripped from water by aeration methods.

As a general rule air stripping appears practical for compounds having a Henry's Law constant of 10^{-3} atm-m^3/mole or higher. Many solvents and other low molecular weight organic compounds have Henry's Law constants in this range. Henry's Law constants, as estimated by EPA for all organic compounds of interest, can be found in Appendix A. Table 7.4.1 lists all those compounds of interest whose estimated Henry's Law constants are in excess of 10^{-3}.

The air stripping rate (rate of mass transfer) can be increased by increasing the magnitude of either the overall mass transfer coefficient or the gas-liquid interfacial area. Both parameters are influenced by the

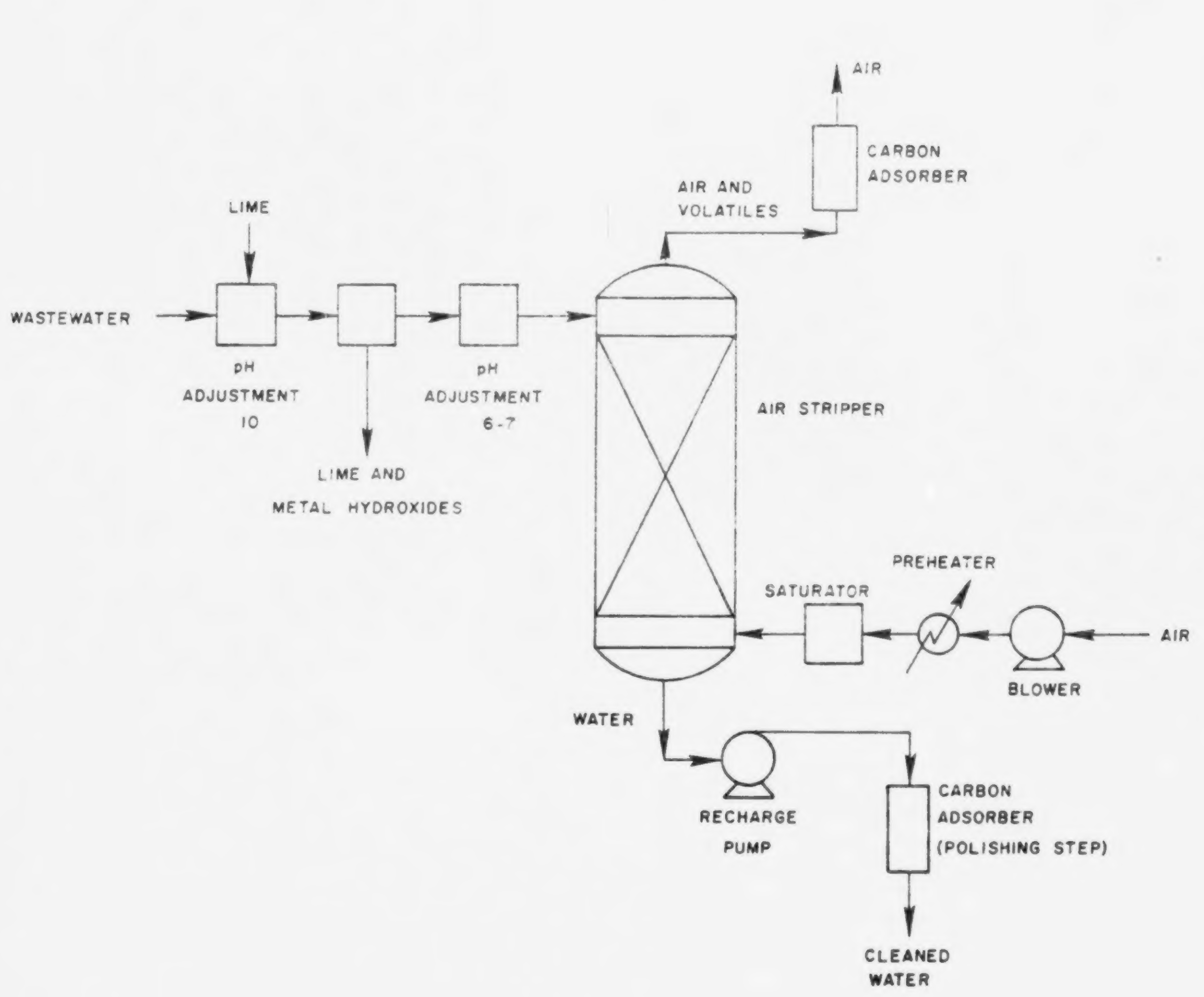

Figure 7.4.2. Air stripping schematic.

TABLE 7.4.1. COMPOUNDS OF INTEREST WITH HENRY'S LAW CONSTANT GREATER THAN 1 X 10^{-3} atm-m^3/mol

COMPOUNDS	HENRY'S LAW CONSTANT
Priority Solvents	
Carbon Disulfide	1.6×10^{-2}
Carbon Tetrachloride	2.1×10^{-2}
Chlorobenzene	3.9×10^{-3}
1,2 Dichlorobenzene	1.9×10^{-3}
Ethylbenzene	8.7×10^{-3}
Methylene Chloride	3.2×10^{-3}
Tetrachlorethylene	2.9×10^{-2}
Toluene	6.7×10^{-3}
1,1,1 Trichloroethane	3.0×10^{-2}
Trichloroethylene	1.0×10^{-2}
Trichloromonofluoromethane	5.8×10^{-2}
1,1,2 Trichloro -1,2,2-Trifluoroethane	4.8×10^{-1}
Xylene	3.0×10^{-3}
Other Organics	
Benzene	5.5×10^{-3}
Chloroform	3.4×10^{-3}
Cyclohexane	1.8×10^{-1}
Dichloro Difluoro Methane	4.0×10^{-1}
1,1-Dichloroethylene	1.9×10^{-1}
1,2-Dichloroethylene	5.3×10^{-3}
1,2-Dichloropropane	2.3×10^{-3}
1,3 Dichloropropanes	1.3×10^{-3}
Ethylene Dichloride	4.3×10^{-3}
Furan	5.7×10^{-3}
Hexachloroethane	2.5×10^{-3}
2-Nitropropane	$1.^{2} \times 10^{-1}$
Chloroacetaldehyde	1.0×10^{-3}
Cumene	1.5×10^{-2}
Methacrylonitrile	3.9×10^{-1}
1-Methylbutadiene	4.2×10^{-2}
Methyl Bromide	5.3×10^{-3}
Methyl Chloride	4.0×10^{-2}

Source: References 2 - 4.

specific engineering design, and the type of aeration system. It is important to note, however, that if mass transfer is controlled by the system's liquid phase resistance, its magnitude is relatively insensitive to changes in gas flow rate. The mass transfer of most compounds amenable to air stripping is usually liquid phase controlled stripping rate mass transfer can be improved most readily by increasing the interfacial area using packed or tray tower air stripping systems.

The optimum design will be that which will achieve effluent concentration goals with the lowest total cost (capital plus operating costs), and is best determined by evaluating a range of values for key parameters. For aqueous wastes containing multiple contaminants, final design criteria will be based on the compoun' whose effluent standard is most difficult to achieve.

In a preliminary design procedure the following information will generally be known:

- waste stream (liquid) flow rate
- compound(s) to be treated
- desired removal efficiency

Using this information along with thermodynamic data, etc., a design determination of the following can be made for tray towers, using a standard chemical engineering text such as Perry (Reference 1).

1. The number of stages theoretically necessary for the required separation,
2. The stage efficiency of the trays relating the theoretical plate to the actual trays,
3. The diameter of the tower necessary to avoid flooding or excessive entrainment, and
4. The pressure drop across the tower.

For packed towers, efficiency is defined as the ability of a system to achieve effective mass transfer between the gas phase and liquid phase. It is inversely related to the height of packing that is equivalent to one transfer unit (HTU). Apart from geometrical consideration related to the shape and arrangement of the packing, the efficiency is affected by viscosity, liquid flow, and Henry's Law constant in more or less the same manner that tray towers are affected.

The design of a packed tower consists of the following steps:

1. Selection of the packing type and size,
2. Calculation of the total height of packing required,
3. Estimation of tower diameter to avoid flooding, and
4. Estimation of the pressure drop.

This procedure involves incorporating several equations and correlations in an iterative fashion to arrive at the optimum system size.

The choice between tray and packed towers is usually made on the basis of least cost of removal. However, there are distinct advantages and disadvantages associated with each type of system. Peters and Timmerhaus[5] present the following comparative merits of both systems:

1. If the operation involves liquids that contain dispersed or suspended solids, use of a tray tower is preferred because the trays are more accessible to cleaning.
2. Random packed towers are seldom designed with diameters larger than 4 feet, and tray towers have diameters that are seldom less than 2 feet.
3. Packed towers are cheaper and easier to construct than tray towers if highly corrosive fluids must be handled. It is easier and cheaper to replace packing periodically than trays.
4. Packed towers are usually preferred for liquids that have a tendency to foam.
5. Liquid holdup is considerably less in packed towers.
6. The pressure drop through packed towers may be less than the pressure drop through tray towers designed for the same duty. This, plus the fact that the packing serves to lessen the possibility of tower wall collapse, makes packed towers particularly desirable for vacuum operations.
7. Tray towers can operate efficiently over a wider range of liquid flow rates that can packed towers.

Other considerations, while not directly related to performance, may have a bearing on the selection. These include the following:

8. Design information for tray towers is generally more readily available and more reliable than that for packed towers.
9. Because of liquid dispersion difficulties in packed towers, the design of tray towers requires less of a safety margin when the liquid to gas ratio is low.
10. Reliable design data for packed towers must often be obtained from experiment.
11. The total weight of a dry tray tower is usually less than that of a packed tower designed for the same duty. However, if liquid holdup during operation is taken into account, then both types of towers have about the same weight.

7.4.1.3 Post-Treatment Requirements--

Post-treatment requirements should be assessed for the treated aqueous stream to ensure that effluent standards have been achieved. The air stream containing the stripped organics should also be examined to ensure that emissions to air are at acceptable levels. Depending upon the concentration of the contaminants in the feed stream and the required air flow rate, the use of a secondary treatment technology (e.g., carbon adsorption, condensation, or direct fume incineration) may be needed to remove the volatile organics from the stripping stream. Collected material may then be recovered or incinerated.

7.4.1.4 Treatment Combinations--

In a wastewater treatment train, stripping is typically the first process step that separates dissolved substances. It follows clarification or filtration steps that are used for removal of suspended solids, and may preceed polishing steps such as biological systems or carbon or resin adsorption. Figure 7.4.2 shows an air stripping treatment train with a variety of pre- and post-treatment options.

The presence of metals such as iron and manganese in the wastewater can cause the precipitation of iron and manganese oxide on the packing material thus reducing the column's operating efficiency. As shown in Figure 7.4.2, a method of pretreating the wastewater involves raising the pH of the feed water to about 10. The metal salts and excess lime used to convert the soluble metals to an insoluble form can then be removed from suspension by gravity settling or filtration. After the metals are removed, adjustment of the water's pH to about 6 or 7 is necessary to reduce the wastewater's corrosive characteristics. The metal containing sludge produced during this precipitation must be removed and treated. Determining the quantity of sludge and its settling, thickening, and dewatering characteristics is necessary for proper design of the treatment train.

Once the water has passed through the stripping column, it may enter into a polishing step to remove residual organics. The most common polishing step is one in which the water is passed through an activated carbon column where adsorption of the remaining contaminants on to the carbon prepares the water for discharge or reuse.

On the air side of the system a preheater may be put on line to warm the air when the air temperature drops below desired levels. Also, depending on the wastes that the system is designed to remove, preheating the air stream (or, more commonly, the aqueous waste stream) may be necessary to affect removal of some of the less volatile compounds in the liquid stream.

As the air enters the column, water will also evaporate from the liquid stream and thus cool the column. To prevent this, an air saturator or humidifier can be added to saturate the air so that the column does not cool due to evaporative losses of water.

As noted, the air leaving the top of the tower containing organics is often allowed to vent to the atmosphere, with the dilute concentrations of organics usually treated by this process posing little threat to air quality. However, if this process were used on a more concentrated waste, some treatment of the exiting air might be required. In this case the air can be vented through a fume incinerator or through a carbon adsorber for removal of the volatiles and then vented to the air.

Apart from the treatment combinations normally used when air stripping represents a primary treatment process, air stripping also occurs in many biological treatment systems. Information available in EPA's Industry Studies Data Base indicates that the total concentration of solvents entering surface impoundments average about 3000 mg/liter and most of these are aerated to assist biological treatment.[2] An appreciable but unknown quantity of these materials are lost through stripping.

7.4.2 Demonstrated Performance

Few data are available on full scale air stripping operations treating industrial effluents. According to information available from EPA's Office of Water there are very few air stripping units dedicated to VOC removal from industrial wastewater's. A 1980 questionnaire sent out to 981 facilities revealed that only five facilities claimed to use air stripping equipment in their wastewater treatment systems. The information and data on these facilities have not been made public knowledge. By far the predominant application of air stripping technology for removal of VOCs is found in the removal of trichloroethane (TCE), and trihalomethanes (THMs) from contaminated ground waters, usually at concentration levels below 1 ppm (see Reference 2 for a discussion of some of the studies). However, some data were found for wastewaters with higher inlet solvent concentrations and are presented below.

7.4.2.1 Pilot Study at IBM's Facility--

A pilot scale air stripping study[6] was done at IBM's 100,000 gallon per day (gpd) zero discharge industrial wastewater treatment facility (IWTF) in Yorktown Heights, NY. The purpose of the study was to determine the effectiveness of a prototype packed air stripping column for removal of larger than trace quantities (1 to 50 mg/l) of volatile organics. The column was constructed of 6 inch diameter pipe packed with 1.5 inch Pall rings to a depth of 6 feet during the study. The stripping column was operated at the facility for several days to determine the effect of liquid flowrate on removal of various solvents. The data in Table 7.4.2 were generated relative to the solvents of interest.

The data show that increasing the liquid flowrate through the column, while holding the gas rate constant, decreases the removal efficiency. Conversely, decreasing the liquid rate, thus increasing the gas/liquid rate, enhances the performance of the stripping column.

7.4.2.2 Bench Scale Mixed Organics Air Stripping Study (Mumford, 1982)--

A bench scale air stripping treatment study was carried out at the Department of Civil Engineering and Environmental Engineering at the University of Iowa.[7] The stripping apparatus consisted of a 4.0 foot high,

TABLE 7.4.2. RESULTS OF PILOT-SCALE AIR STRIPPING STUDY

Q, gpm/ft^2 G/L[a]	4.1 184		5.8 130		8.2 83		13.3 45		15.3 39		23 24	
	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal
Acetone	14	20	41	27	18	8	6	16	6	18	20	-29
	--		44	29	24	26	8	6	5	15	32	24
Tetrachloroethylene	--	--	--	--	--	--	--	--	--	--	11	83
	--	--	--	--	--	--	--	--	--	--	7	80
Toluene	--	--	--	--	--	--	--	--	--	--	3	79
	--	--	--	--	--	--	--	--	--	--	2	81
Trichloroethylene	0.9	98	4	89	3	88	1	86	2	67	2	79
	--	--	7	90	2	87	2	92	1	99	2	88

[a] Gas/Liquid Ratio, By Volume

Source: Reference 6.

3.75 inch ID plexiglas column. The column was packed with 1.5 feet of 1/4 inch Berl saddles. The system was operated at gas/liquid ratios ranging from 25 to 300. Table 7.4.3 presents the influent concentration and percent removal of selected compounds relevant to this study. In general, the study showed that removal efficiencies, for a constant gas to liquid ratio, were highest for compounds with high Henry's Law constants. The data also showed that as gas to liquid ratio increases, the percent removal also increases. At even higher ratios, it is anticipated that the percent removal will level off due to the influence of liquid phase mass transfer resistance. Column flooding will also occur when the gas to liquid ratio exceeds design criteria.

7.4.2.3 Pilot Scale Air Stripping Treatability Study--

A pilot scale air stripping system was constructed to investigate the feasibility of air stripping volatiles from a contaminated ground water supply.[8] The system consisted of a 3-1/8 inch x 48 inch glass stripping column that was packed to a depth of 26 inches with 7 mm glass Rashig rings. Six runs were made at different air and water feed rates and Table 7.4.4 presents the data generated. This study showed surprisingly poor removal efficiencies for TCE in comparison to other published reports. The authors noted that the formation of iron and manganese oxide on the packing material affected the performance of the system; although it does not appear that this would affect the volatility of TCE relative to the other compounds studied.

7.4.3 Cost of Treatment

As mentioned earlier, the optimum design for an air stripping system will be that which involves the least cost for the desired removal efficiency. The total cost is divided into two categories: (1) capital costs, and (2) operating costs. Capital costs can be estimated using methods described by Peters and Timmerhaus.[5] The capital cost is broken down into three parts: (1) tower shell costs, including heads, skirts, and nozzles, (2) internal element costs, including packing, supports, and distributor plates, and (3) auxiliaries costs, including platforms, ladders and handrails. Using the tables and curves presented in Reference 5, one can arrive at a capital cost estimate for a variety of column and packing

TABLE 7.4.3. RESULTS OF BENCH-SCALE AIR STRIPPING STUDY

G/L Ratio[a] $L(m^3m^2\text{-}hr)$	25 10.3		50 11.3		100 7.81		200 3.98	
Solvent	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal	Inlet ppm	% Removal
Carbon Tetrachloride	5.4	69	84.2	82	67.4	89	15.3	87
Toluene	3.4	74	5.3	77	37.1	93	2.7	96
Chlorobenzene	13.3	65	9.2	72	7.8	77	3.6	97
1,2-Dichlorobenzene	14.2	60	27.8	70	24.0	74	11.0	94
Nitrobenzene	4.2	5	111	11	115	16	3.9	28

[a] Gas/Liquid Ratio, by Volume.

Source: Reference 7.

TABLE 7.4.4. RESULTS OF PILOT-SCALE AIR STRIPPING TREATABILITY STUDY

Gas to Liquid Ratio		53	26	54	107	396	9
L, liters/m		0.75	0.75	0.37	0.37	0.1	0.75
	Raw Water	% Removal					
Compound	ppm	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1,1,1-Trichloroethane	150	65	56	60	74	95	56
Trichloroethylene (TCE)	338	0	9	9	--	44	9
Methyl Isobutyl Ketone	76	41	21	68	43	75	21
Toluene	92	67	75	79	81	92	51
Ethylbenzene	24	99	99	98	98	99	96
Benzene	69	48	--	--	--	--	0
Tetrahydrofuran	22	ND	--	--	--	--	ND

ND = Not Detected.

Source: Reference 8.

materials. Cost estimates can vary greatly depending on the diameter and height of tower needed, the depth and type of packing, and the material of construction. The operating cost for an air stripping system is also related to the complexity of the pre- and post-treatment options necessary to operate the system as well as the operating parameters of the column itself. Operating costs that are specifically associated with the stripping operation are incurred from the electricity required to run the liquid feed pump and the air blower.

Some data are available from a field operation in Wisconsin where in 1984 an air stripping column was constructed to remove VOCs from contaminated ground water.[9]. The system treats an average of 2 million gallons of ground water a day with about a 98 percent VOC removal efficiency. Data covering the first 5 months of operation show the cost of treatment to be about 5.11 cents per 1,000 gallons of water treated. The tower is reported to have cost roughly 104,000 dollars to install. Operating costs were about 33,000 dollars per year, including 14,000, 16,000, and 3,300 dollars per year for capital, operating and maintenance costs, respectively.

7.4.4 Overall Status of Process

7.4.4.1 Availability--

The use of air stripping as a primary treatment process for the removal of volatile organics from water streams is relatively new and is generally used only for dilute concentrations. However, equipment suitable for almost any application is available from a number of vendors specializing in the design and sale of vapor-liquid contacting equipment. The Chemical Engineering Buyers' Guide[10], for example, identifies about 100 manufacturers who custom design tower equipment for contacting operations including air stripping and similar applications. Another 50 or so firms are involved in supplying aeration equipment for vapor-liquid contacting. Some bench or pilot scale activity will undoubtedly be required to establish design requirements for equipment for specific waste stream applications.

7.4.4.2 Application--

As noted in Reference 2, air stripping may not achieve very low concentrations of volatile solvents present above 5 mg/liter, even at high air-to-water ratios. It is suggested in Reference 2 that air stripping may be useful in treating water containing volatiles at low concentrations; or in treating higher concentrations of volatiles prior to further treatment, such as biological treatment. Steam stripping should probably be considered a more effective process for higher concentrations of solvents, particularly those that are less volatile.

7.4.4.3 Environmental Impact--

Consideration of the environmental impact of air stripping processes should focus on assessing the concentration levels of the air/water primary process streams. Additional treatment may be indicated. Residuals from secondary treatment (e.g. activated carbon adsorption) may pose additional treatment or disposal requirements, as would residuals from pretreatment operations to remove solids and metals from waste stream feedstocks.

7.4.4.4 Advantages and Limitations--

The principal advantage of air stripping is its simplicity and inherently low cost. However, increases in processing time and the inclusion of design features aimed at improving mass transfer efficiency may add appreciably to the cost. The needs for offgas treatment could have a significant influence on column design and on overall process economic viability. Air stripping is most cost effective as a final polishing treatment for aqueous wastes with low (e.g., less than 5 ppm) VOC concentrations. At higher inlet concentration, it may be used as a pretreatment process followed by biological treatment or carbon/resin adsorption.

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7.5 LIQUID - LIQUID EXTRACTION

Liquid - liquid extraction is the separation of constituents of a liquid solution by transfer to a second liquid, immiscible in the first liquid, but for which the constituents have a preferential affinity. Although not a commonly used treatment technology, liquid extraction has potential for removal of many organic constituents from effluent waste streams. Liquid extraction can be attractive in cases where the solutes in question are toxic or non-biodegradable, where the solutes are present at high enough concentration levels to provide economic recovery value, when steam stripping would be rendered less effective by low solute volatility or formation of azeotropes, or when high concentrations increase activated carbon adsorption costs to excessive levels. Historically, its application to wastewater treatment generally has been limited to removal of phenol and phenolic compounds present at high concentration (5% or greater). Steam stripping is not very effective on phenolic compounds because of low Henry's Law constants and activated carbon adsorption is not feasible at these high concentrations.

7.5.1 Process Description

The liquid-liquid extraction process is shown in Figure 7.5.1. The process includes typically the following basic steps:

1. extraction of organic pollutants from wastewater,
2. recovery of solute from the solvent phase, or extract,
3. removal of solvent from treated wastewater, or raffinate.

The first step, extraction brings two liquid phases (feed and solvent) into intimate contact to allow transfer of solute from the feed to the solvent. Any method by which single or multistage mass-transfer processes can be conducted can conceivably be used to conduct liquid extractions. For example, an extractor unit can be a mixer-settler device in which feed and solvent are mixed by agitation, then allowed to settle and separate into two

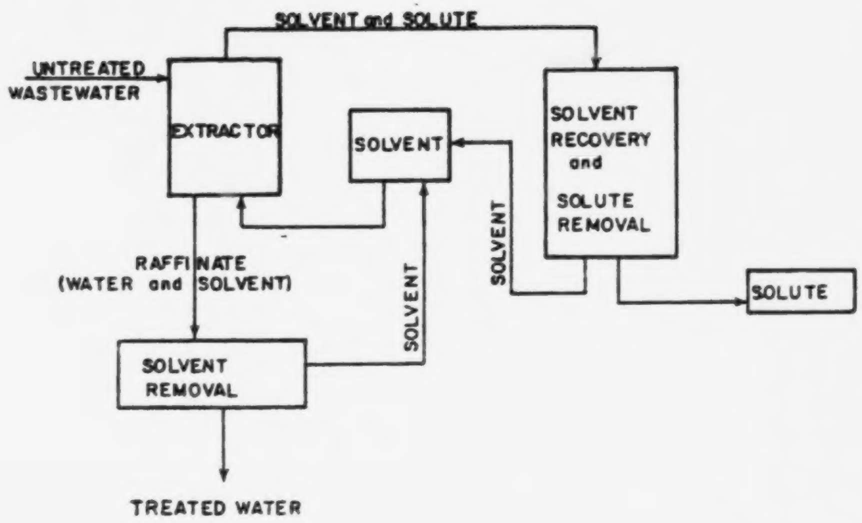

Figure 7.5.1. Schematic of extraction process.

liquid streams; or it can be a column in which two liquids are brought into contact by counter-current flow caused by density differences. The process yields two streams, the cleaned stream or raffinate and the extract or solute-laden solvent stream.

The second step, solvent regeneration, can be accomplished by a second extraction or distillation. For example, a second extraction, with caustic, is sometimes used to extract phenol from light oil, which is used as the primary solvent in dephenolizing coke plant wastewaters. However, distillation is much more common. Potential difficulties with distillation might arise if azeotropes are present, or if the relative volatilities of the solvent and the extracted compound are close enough to hinder separation.

The third step, removal of solvent in the treated wastewater or raffinate is necessary when solvent concentrations are great enough to create solvent losses that would add significantly to the process cost or have a detrimental environmental impact. This can be accomplished by a number of technology options. When treating large quantities of dilute wastes, an additional extraction step usually cannot compete on an economic basis with other technologies such as stripping, biological or adsorption post-treatments.

7.5.1.1 Pretreatment Requirements for Different Waste Forms and Characteristics--

Pretreatment is necessary to remove material which will interfere with the mass transfer of the organic contaminant into the solvent extract and which will require higher solvent/aqueous phase ratios to obtain desired levels of extraction. Thus, any emulsion or organic phase droplets should be removed by any one of several pretreatment options. Solids, to the extent that they retain sorbed contaminants or hamper column performance, should be removed. In certain cases dissolved solids can also affect partitioning of the solute(s), and removal or addition of material may be desirable to enhance the separation. Similarly, changes in temperature may also modify partitioning behavior. Distribution data, if not available in the literature, will generally have to be developed in the laboratory, although an estimation method based on vapor liquid data for binary systems can be used to estimate the distribution of an organic compound (at low concentrations) between water and an organic solvent. (See Section 15 of the Sixth Edition of the Chemical Engineers' Handbook by Perry, et al.)[1]

7.5.1.2 Operating Parameters--

Liquid extractions may be carried out in various ways. In the simplest case the solvent is added to a liquid mixture, causing a second liquid phase to form. It may be desirable to add a salt to an aqueous phase to enhance the activity of a component, causing it to transfer into a nonaqueous phase in which the salt is insoluble. It may also be desirable to adjust the pH of an aqueous phase containing organic acidic or basic solutes to depress their ionization and cause them to concentrate in the nonaqueous solvent phase. It is often helpful to change the temperature of the phases in contact to give the most favorable equilibrium at each step of the extraction.

Theoretically, any aqueous organic waste can be treated by extraction. However, determining potential feasibility requires a series of analyses to assess overall system practicality. Much depends on how residual solvent is to be removed from the treated water stream, how the solvent is to be regenerated, and what restrictions exist for each unit operation.

In general, extraction is best suited for waste streams of consistent composition to assure satisfactory performance. In cases where performance is less important, acceptable ranges in waste characteristics become a little broader, as in the case where extraction is to be used as a pretreatment. For example, when several waste streams are to be combined for final treatment, a single waste stream with higher constituent concentration may be extracted to reduce the load on the final treatment process.

As noted in Perry's Chemical Engineers' Handbook, the removal mechanisms in extraction are primarily physical, since the solutes being transferred are ordinarily recovered without chemical change. On the other hand, the physical equilibrium relationship on which such operations are based depend mainly on the chemical characteristics of the solutes and solvents. Thus, use of a solvent that chemically resembles one component of a mixture more than the other components will lead to concentration of that like component in the solvent phase, with the exclusion from that phase of the dissimilar components.

The choice of solvent is a key factor in evaluating the utility of liquid extraction as a means of removing hazardous organic compounds from aqueous waste streams. Perry, et al.[1] lists characteristics which must be assessed in selecting a solvent. These are:

- Selectivity-the ability of a solvent to extract the organic contaminant preferentially from the aqueous phase. It is a numerical measure that is equal to the ratio of the distribution constants of contaminant and water in the solvent. As such, it is analogous to relative volatility as used in distillation. Poor selectivity (ratios near unity) means large solvent feed ratios and a large number of extraction stages will be needed for good separation.

- Recoverability-the solvent must be recoverable from both extract and raffinate. Since distillation is the usual recovery method, relative volatilities of all components should be favorable and low latent heats for volatile solvents are desirable.

- Distribution Coefficient-the distribution coefficient of the contaminant should be large in order to achieve selectivity and reduce equipment size and costs.

- Contaminant Solubility-the solubility of the extracted contaminant in the solvent should be high in order to reduce solvent requirements.

- Solvent Solubility-the solubility of the solvent in the aqueous phase should be low. This will generally increase selectivity, the range of waste stream concentrations that can be handled, and reduce costs of solvent recovery or makeup.

- Density-a difference in density is essential since the flow rates and separation of the two phases is directly affected.

- Interfacial Tension-the interfacial tension should be large to assist in the coalescence of dispersed phase droplets.

- Other-other desirable solvent properties are low corrosivity, low viscosity for higher mass transfer rates, nonflammability, low toxicity, and low cost.

Binary critical solution temperatures of solute components with prospective solvents is suggested as a guide to solvent selection. The solvent having the lower critical solution temperature with the solute compound will be more selective in an extraction from the aqueous phase.[1]

A significant quantity of data have been collected for the distribution of pollutants in water and various extractive solvents. These values, called equilibrium distribution coefficients (K_D), generally express the equilibrium concentration of the solute as the ratio of the weight percent in solvent relative to water. It can also be expressed as mole or volume fraction ratios.

$$K_D = \frac{X_{os}}{X_{oa}}$$

where: X_{os} the weight fraction of organic solute in the solvent phase and

X_{oa} is the weight fraction of organic solute in the aqueous phase, both at equilibrium.

K_D values for the octanol/water system for solvents and other low molecular weight organic compounds of interest are provided in Appendix A. These data represent just a small fraction of the data available in the literature for ternary systems consisting of water and two organic compounds. For example, a number of references are provided in Perry[1] along with distribution coefficients for over 200 selected water/organic solute/organic solvent systems which include many of the organic compounds of concern. Values of K_D that are specific to the compounds of concern are provided in a number of recent publications. These data, of use in assessing the potential of liquid-liquid extractions as a treatment technology are provided in Tables 7.5.1 through 7.5.4. The data in Table 7.5.1 were reported in the AIChE Symposium Series (1981) by S. T. Hwang.[2] The basic references used are provided in the table. Tables 7.5.2 through 7.5.4 report K_D data from a two-part University of California, Berkeley report published by the EPA (see Reference 8).

Higher values of K_D mean that less solvent is required to extract a given amount of solute from the wastewater and thereby usually leads to less expensive extraction processes. The ratio of the distribution coefficients of solvent systems for extraction of a specific solvent from water is a measure of the relative amounts of solvent that must be employed to achieve a given level of extraction. However, distribution coefficients are only one of the many solvent properties that must be considered.

The Chemical Engineers' Handbook, Kirk Othmer (Reference 9) and other background materials present calculation and design methods that can be used to assess the applicability of liquid-liquid extraction to specific waste streams. The techniques generally involve the use of equilibrium distribution data to develop equilibrium and operating line curves which can be used to provide graphical calculations of the number of theoretical stages required to

TABLE 7.5.1. K_V VALUES FOR AQUEOUS/SOLVENT SYSTEMS[a]

Solute	Solvent										
	Tricresyl phosphate	Undecane	MIBK	Tridecane	Benzene	Isobutylene	Isobutane	n-butyl acetate	Isobutyl acetate	Diisopropyl ether	Octanol
acrolein	0.1**	1*	2*	1*	2*	1*	1*	2*	2*	1*	0.1*
benzene	132**	166**	150*	40*	518(7)	242(3)	186(3)	54(3,7)	54**	54**	160(3)
carbon tetrachloride	480**	380*	930*	300*	2,200*	1,200*	810*	870*	900*	990*	436
chlorobenzene	250*	260*	1,200*	200*	2,900*	685*	445*	1,200*	1,060*	460*	692
1,2-dichloroethane	31**	10*	38*	8*	100*	41(3)	24(3)	37*	36*	32*	38
1,1,1-trichloroethane	81**	120*	220*	110*	270*	190*	150*	210*	210*	150*	92**
hexachloroethane	11,000*	3,500*	9,600*	2,500*	62,000*	8,600*	5,300*	9,400*	9,000*	7,600*	8,800*
1,1-dichloroethane	51*	56*	140*	52*	100*	94*	70*	140*	130*	68*	138*
1,1,2-trichloroethane	74*	70*	220*	64*	200*	110*	80*	210*	200*	86*	224*
chloroethane	28**	31*	62*	30*	43*	50*	40*	60*	60*	37*	35**
bis(2-chloroethyl) ether	21*	19*	90*	17*	82*	36*	22*	90*	80*	24*	94*
chloroform	80**	46*	117*	44*	88*	76*	57*	116*	111*	56*	93*(6)
1,2-dichlorobenzene	2,700**	1,900*	3,800*	1,600*	11,000*	2,300*	1,600*	3,800*	3,500*	2,300*	2,400**
1,1-dichloroethylene	1,100**	-1,000*	1,200*	900*	2,750*	1,200*	960*	1,100*	1,200*	1,150*	999*
1,2-trans-dichloroethylene	770**	260*	840*	210*	1,500*	710*	510*	810*	810*	830*	738*
1,2-dichloropropane	120*	125*	330*	114*	275*	200*	150*	320*	340*	150*	305*
1,3-dichloropropylene	120*	130*	450*	120*	370*	230*	160*	450*	420*	150*	474*
ethylbenzene	1,300*	660*	1,200*	490*	5,700*	2,060*	1,300*	1,200*	1,200*	1,200*	1,412(5)
methylene chloride	13*	15*	50*	12*	106*	36*	26*	50*	46*	24*	72*
methyl chloride	9*	10*	18*	9*	14*	14*	11*	18*	17*	11*	30*
methyl bromide	432*	460*	960*	450*	750*	680*	550*	960*	930*	530*	1,000*
bromoform	143*	140*	530*	130*	500*	240*	160*	540*	490*	160*	610*
trichlorofluoromethane	563*	690*	980*	650*	770*	1,120*	950*	939*	955*	850*	740*
dichlorodifluoromethane	2,400*	7,400*	6,700*	6,000*	5,300*	38,000*	33,000*	5,000*	6,330*	15,000*	4,500*
nitrobenzene	61**	55*	250*	47*	460*	72*	44*	260*	230*	97*	71(6)
tetrachloroethylene	1,300*	1,460*	6,300*	1,100*	14,000*	4,000*	2,600*	6,150*	5,500*	2,600*	4,500*
toluene	540***	1,200*	730*	230*	2,350*	1,004(3)	801(3)	690*	700*	730*	537(5)
trichloroethylene	280*	170*	900*	306*	675*	570*	416*	900*	860*	370*	882*

(continued)

TABLE 7.5.1 (continued)

Solute	Solvent Cumene	Mesityl oxide	MEK	Ethyl acetate	Ethyl ether	Ethyl benzene	n-hexanol	Ethylene Dichloride	Toluene	Xylene	n-hexane
acrolein	1*	3*	4*	3*	2*	2*	3*	1*	2*	3*	1*
benzene	263*	130*	114*	109*	174*	218*	45*	473*	271*	360*	116*
benzidine	85*	66*	78*	70*	131*	86*	16*	65*	98*	136*	101*
carbon tetrachloride	1,460*	770*	690*	668*	1,200*	1,266*	236*	2,329*	1,570*	2,069*	866*
chlorobenzene	1,080*	1,700*	3,480*	2,360*	1,000*	1,450*	1,180*	3,700*	1,660*	2,500*	610*
1,2-dichloroethane	72*	34*	30*	28*	40*	55*	14*	142*	70*	92*	24*
1,1,1-trichloroethane	196*	212*	221*	208*	239*	22*	96*	212*	248*	388*	177*
hexachloroethane	2.4×10^4	8,183*	6,600*	6,100*	1×10^4*	2.8×10^4*	1,184*	9×10^4*	3.7×10^4*	4.7×10^4*	8,600*
1,1-dichloroethane	66*	163*	200*	186*	127*	93*	130*	55*	101*	163*	73*
1,1,2-trichloroethane	108*	256*	309*	278*	174*	165*	202*	115*	184*	290*	95*
chloroethane	33*	67*	79*	75*	61*	40*	50*	25*	43*	70*	39
bis(2-chloroethyl) ether	34*	114*	148*	129*	63*	64*	92*	38*	72*	110*	28
chloroform	56*	134*	162*	150*	103*	79*	109*	48.3*	86*	138*	60*
1,1-dichloroethylene	1,900*	990*	870*	840*	1,360*	2,127*	359*	2,770*	2,400*	3,800*	1,330*
1,2-trans-dichloro-ethylene	1,300*	738*	665*	640*	982*	903*	294*	1,768*	1,100*	1,488*	562*
1,2-dichloropropane	170*	369*	440*	404*	298*	234*	250*	158.8*	259*	407*	170*
1,3-dichloropropylene	168*	555*	703*	632*	333*	315*	492*	180*	246.8*	548*	178
ethylbenzene	2,480*	995*	840*	797*	1,570*	2,940*	230*	6,070*	3,700*	4,700*	1,400
methylene chloride	46*	69*	106*	89*	45*	59*	58*	134*	68*	103*	30*
methyl chloride	10*	20*	24*	22*	16*	14*	20*	9*	15*	24*	11*
methyl bromide	509*	1,090*	1,300*	1,220*	846*	700*	1,049*	434*	751*	1,249*	550*
bromoform	208*	682*	880*	778*	366*	418*	696*	238*	462*	734*	188*
trichlorofluoro-methane	701*	925*	1,000*	975*	1,200*	718*	454*	503*	773*	1,249*	894*
dichlorodifluoro-methane	5,127*	4,180*	4,600*	23,000*	2.1×10^4*	4,573*	269*	2,578*	4,500*	7,380*	14,880*
nitrobenzene	246*	309*	349*	298*	176*	309*	270*	353*	363*	550*	80*
toluene	1,300*	606*	527*	506*	919*	1,290*	170*	2,674*	1,690*	2,080*	708**
trichloroethylene	375*	1,074*	1,320*	1,220*	771*	595*	840*	344*	650*	1,030*	436*

*Estimated from solubility parameters.

**Estimated using the method in Reference 4.

Other reference numbers in ().

$$^{a}K_V = K_D \times \frac{\text{Specific Gravity of Solvent}}{\text{Specific Gravity of Water}} = \frac{\text{Grams Solute/1,000 ml Solvent}}{\text{Grams Solute/1,000 ml Water}}$$

TABLE 7.5.2. EXPERIMENTALLY MEASURED EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR EXTRACTION FROM WATER INTO UNDECANE, (295-300 K) AND 1-OCTANOL

Solute	K_D Undecane	K_D 1-octanol
Benzene	214	160
Toluene	740	196
Ethylbenzene	2,500	1,710
Chlorobenzene	845	838
1,2-Dichlorobenzene	3,030	3,040
Chloroform	75	96
Carbon tetrachloride	738	650
1,1,1-trichloroethane	414	357
1,1,2,2-tetrachloroethane	110	297
1,2-dichloropropane	74	---
1,2-trans-dichloroethylene	119	318
Trichloroethylene	354	409
Tetrachloroethylene	2,700	---
Bromoform	127	---

Source: References 3 and 8.

TABLE 7.5.3. MEASURED VALUES OF K_D FOR EXTRACTION OF ACROLEIN FROM WATER INTO VARIOUS SOLVENTS

Solvent	Measured K_D
Alcohols	
2-ethylhexanol	1.25
2-ethyl-1,3-hexanediol	1.41, 1.59
Carboxylic Acids	
2-ethylhexanoic acid	0.45, 0.59
Naphthenic acids	0.62, 0.62
Alkane	
Undecane	0.47, 0.41
Chlorinated Organics	
Methylene chloride	6.6
Tetrachloroethylene	0.54
1,2-dichloroethane	3.75
1,1,2-trichloroethane	3.45
1,1,2,2-tetrachloroethane	4.6
Aromatics	
Toluene	2.05, 2.25
Styrene	2.46, 2.53
Nitrobenzene	2.68, 2.58
Olefins and Terpenes	
1,5-cyclooctadiene	0.54
Turpentine	0.39, 0.43
Esters	
n-hexyl acetate	1.99, 2.17
n-butyl acetate	2.38, 2.75
n-octyl acetate	1.71
Ether	
di-n-butyl ether	1.06, 1.09
Diisopropyl ether	1.7

(continued)

TABLE 7.5.3 (continued)

Solvent	Measured K_D
Ketones	
Isobutyl heptyl ketone (IBHK)	0.93
Methyl isobutyl ketone (MIBL)	4.90, 4.91, 4.84
Mesityl oxide	3.01, 5.02
Diisobutyl ketone (DIBK)	1.57, 1.63
5,5-dimethyl-1,1,3-cyclohexanodione;	
-saturated in 2-ethylhexanol	5.78, 5.9, 3.15
-saturated in DIBK	2.66, 2.15
Furan	
2-methyl furan (99% pure)	2.66, 2.23
2-methyl furan, with up to 10% methyl tetrahydrofuran	8.4, 17.4, 9.29
Phosphoryl Compounds	
Tributyl phosphate (TRP)	1.97, 1.99
Tricresyl phosphate (TCP)	1.77, 1.68
Di-2-ethylhexyl phosphoric acid	1.72, 1.04
22.1% w/w trioctyl phosphine oxide (TOPO) in DIBK	2.06, 1.63
Others	
Ethyl propionate	1.5
Isobutyl isobutyrate	1.98
Nitropropane	3.6

Source: Reference 8

TABLE 7.5.4. MEASURED EQUILIBRIUM DISTRIBUTION COEFFICIENTS (K_D) AT 30°C FOR EXTRACTION OF NITROBENZENE FROM WATER INTO VARIOUS SOLVENTS

Solvent	Solvent/ feed (v/v)	Feed concentrations, ppm (w/w)	K_D
Undecane	0.25	1,206	36
	0.25	1,206	39
	0.25	1,206	37
Toluene	0.03	965	352
	0.03	1,206	353
	0.03	1,206	353
DIBK	0.10	503	277
	0.10	1,206	278
	0.10	1,206	301
	0.15	1,206	270
TBP (tri butyl phosphate)	0.10	603	269
	0.10	603	297
	0.10	1,206	277
	0.10	1,206	289
	0.10	1,206	310
MIBK	0.05	1,206	244
	0.05	1,206	217
	0.10	1,206	204

achieve desired extraction levels. The general method is analogous to the use of McCabe-Thiele diagrams to assess distillation performance. Formulas, such as the Kremser equations, are also available that quantitatively express the effect of flow variations on exit concentration levels. The use of such techniques (in conjunction with laboratory data) will provide the basis for determining equipment size and post-treatment requirements and, therefore, the costs and applicability of the liquid extraction process.

7.5.1.3 Post-Treatment Requirements--

The post-treatment requirements of a liquid-liquid extraction process will be determined by many of the system component properties discussed above, e.g., solvent solubility in the aqueous phase will determine the need for further treatment to eliminate solvent discharge with the treated waste stream; and the relative volatilities of the solute and solvent will affect the ease of their separation following extraction. These operations could be considered to be process steps as opposed to post-treatment steps, and careful selection of solvent and proper design can minimize the cost and difficulty of such processes. Given the necessity for post-treatment, those technologies most commonly used for raffinate are established technologies such as steam/air stripping, carbon adsorption, and biological treatment. Distillation will probably be used to separate solvent and solute. These technologies are discussed in some detail in other sections of the report.

7.5.2 Demonstrated Performance

The use of liquid-liquid extraction for the treatment of aqueous organic waste streams has been limited. Application of the technology has been primarily for the treatment of phenol contaminated waste streams from the petroleum and coal processing industries. Because of difficulties involved in removal of phenol from these specific waste streams by steam stripping and adsorption, liquid-liquid extraction has proven to be particularly well suited.

Since the scope of this document does not include phenols, actual performance data in the field are limited to a series of pilot runs. Most of the research was conducted under EPA auspices to assess the extractability of priority pollutants from industrial waste streams. Results of these studies are summarized below.

7.5.2.1 Results of Study #1; Reference 10, Earhart, S.P., et al. (1976)--

Solvent extraction was explored in this EPA sponsored program as a method of treating wastewaters from petroleum refineries and petrochemical plants. Waste constituents included solvents covered in this report. Results were obtained from the use of both spray columns and rotating disc contactors (RDC).

7.5.2.1.1 Results From Spray Column Extractor--The primary objective of experiments conducted in the spray column was to prove the overall process feasibility of volatile liquid extraction. Several types of organic chemicals were extracted. Most of these solutes are known to be present in the wastewater from chemical processing plants, but they were also chosen to determine if any class of organic chemicals might cause unexpected problems such as an irreversible reaction with isobutylene and the other extraction solvents tested. Most of the solutes studied were present in synthetically prepared water solutions, but industrial samples of lube oil refining wastewater and cresylic acid recovery wastewater were also tested.

The data, which were measured at steady state in each run included the solvent and water flow rates, the temperatures of the two streams leaving the extractor, and the concentrations of each solute in the feed and product water. Other variables measured included, component viscosity and density, phase velocity, interfacial area per column volume, percent of flooding, and dispersing phase rise (or fall) time. Typical variables recorded during the study are shown in Table 7.5.5. Details can be found in the reference for specific runs. Results for several solvent/contaminant combinations were reported, as summarized in Table 7.5.6. As shown in the table, average effluent product water contaminant concentrations were 10 mg/liter or more.

7.5.2.1.2 Results from RDC extractor--Steady state data obtained in the study included the solvent and water flow rates, the diameters of the discs and stator holes, the compartment heights and column height, the rotational speed of the discs, the temperatures of the two streams leaving the RDC, and the concentrations of each solute in the feed and product water. In some experiments the solvent hold up, and the solute concentrations in the loaded solvent, were also measured.

TABLE 7.5.5. VARIABLE MEASURED IN SPRAY COLUMN EXTRACTOR STUDY

Spray Column Run #1 Temperature = 22.7°C

Dispersed Phase = Isobutylene

Continuous Phase = Prepared waste water

Priority Constituents = o-cresol

V_d = 82.43 ft/hr, V_c = 19.38 ft/hr, F_s/F_w = 2.519

ρ_d = 0.5908 gm/cc, ζ_d = 0.180 cp,

ρ_c = 0.9976 gm/cc, ζ_c = 0.942 cp,

d_p =.01865 inch, a = 17.11 ft^2/ft^3

FF = 15.3%, RT = 6.78 seconds

Solute	K_D	Feed water (ppm)	Product water (ppm)	Percent removal
1. Phenol	0.70	20,000	4,180	79.1
2. O-cresol	4.80	10,000	492	95.1

V_d = dispersed phase velocity
V_c = continuous phase velocity
F_s/F_w = solvent mass flow rate/water mass flow rate
ρ_d = density of dispersal phase
ρ_c = density of continuous phase
ζ_d = viscosity of dispersal phase
ζ_c = viscosity of continuous phase
d_p = drop diameter
a = interfacial area per column volume
FF = percentage of flooding
RT = dispersed phase rise (or fall) time
K_D = equilibrium distribution coefficient

TABLE 7.5.6. RESULTS OF SPRAY COLUMN EXTRACTOR RUNS

Wastewater/solvent contaminant	K_D	Number of runs	F_s/F_w range[a]	Feed water[b] (ppm)	Product water[b] (ppm)	Removal (percent)	Removal range (percent)
Prepared Wastewater/Isobutylene							
Phenol	0.7	4	1.381 to 2.519	18,150	3,260	82	76 to 82
Acetone	0.63	6	0.686 to 2.189	2,050	1,025	50	28 to 74
Benzene	407	2	0.686 to 1.833	295	13	97	93 to 98
n-butanol	0.76	4	0.686 to 2.624	5,204	1,420	63	35 to 88
n-butyl acetate	168	6	0.686 to 2.184	2,125	150	93	76 to 98
o-cresol	4.8	4	1.381 to 2.519	3,550	165	95	95 to 97
ethylene dichloride	70	4	0.198 to 2.189	2,980	510	83	62 to 93
methyl ethyl ketone	2.49	4	1.330 to 2.189	3,390	1,090	68	62 to 78
Prepared Wastewater/n-butane							
Ethylene dichloride	44	3	0.189 to 0.475	2,890	1,190	59	43 to 75
Cresylic Acid Recovery Wastewater/Isobutylene							
Phenol	0.7	1	1.785	579	163	72	—
o-cresol	4.8	1	1.785	327	31	90	—
m p-cresol	2.7	1	1.785	291	25	91	—
xylenols	7.0	1	1.785	227	10	96	—
Lube Oil Refining Wastewater/Isobutylene							
Phenol	0.7	3	1.429 to 2.535	21,150	8,080	62	41 to 80
Acetone	0.63	2	1.429 to 2.535	37	19	49	41 to 57
Benzene	407	2	1.429 to 2.535	170	21	88	80 to 96
o-cresol	4.8	2	1.429 to 2.535	232	2040	91	84 to 98
methy ethyl ketone	2.49	2	1.429 to 2.535	232	39	84	76 to 95

[a] F_s/F_w = solvent mass flow rate/water mass flow rate.
[b] Average values.

Source: Earhart, J.P., et al. (1976), Reference 10.

During the second portion of the experimental program, several prepared aqueous solutions and industrial wastewaters were treated by extraction in the RDC as described in Reference 10. Experiments included runs using volatile solvents, less volatile polar solvents, and mixtures of volatile and polar solvents. In these experiments the solvent was always the dispersed phase, and the solvent to water flow ratio (F_s/F_w) was set at much lower values (i.e., ratio ranged from 0.1 to 0.3) in order to demonstrate solvent extraction under conditions which would be most likely to lead to favorable process economics.

In addition to the choices of solvent and the value of F_s/F_w, the independent variables which could be varied on the RDC included the water flow rate, the disc rotational speed, the disc diameter, the stator hole diameter, and the compartment height. The principal measured responses were the solvent hold up, the concentrations of each solute in the treated water, and in most runs, the concentration of each solute in the loaded solvent. The temperature (ambient 21°C) was measured but not controlled. Results for several runs are summarized in Table 7.5.7. Full details concerning all data collected during the test study are available in Earhart, et al. (1976). The removal efficiencies are generally similar to those obtained in the spray column studies.

7.5.2.2 Results of Study #2: Ricker and King, 1980, Reference 11--

Using the same rotating disc contactor pilot equipment for runs conducted by Earhart, et al. (1976), a solvent extraction study of wastewaters from acetic acid manufacturers was performed by University of California, Berkeley staff members and was published in 1980 as EPA Report 600/2-80-064. The test conditions studied and the results of a test run are shown in Table 7.5.8. Waste constituents studied included those shown in the table plus a variety of other low molecular weight organic acids, alcohols, aldehydes, and ketones. Solvents included 2-ethyl hexanol, n-amyl alcohol, cyclohexanone, 2-heptanone, and diisobutylketone. Removal efficiencies for all materials tested fell within the range shown in Table 7.5.8. Contaminant concentrations in the treated raffinates (water phases) were generally high enough to require some form of post treatment.

TABLE 7.5.7. RESULTS OF RDC EXTRACTOR RUNS

Wastewater/solvent contaminant	K_D	F_s/F_w range[a]	Feed water[b] (ppm)	Product water[b] (ppm)	Removal (percent)	Removal range[c] (percent)
Prepared Wastewater/Isobutylene						
Phenol	0.70	0.0996	605	522	13.7	--
Acetone	0.63	0.0996	29.9	28.2	5.7	--
Benzene	407	0.0996	68.5	60.4	11.8	--
n-butyl acetate	168	0.0996 to 0.3538	4,050	125	97	93 to 99
o-cresol	4.8	0.0996	72.8	17	76.6	--
methyl ethyl ketone	2.49	0.0996 to 0.3538	1,450	660	54	23 to 70
Prepared Wastewater/n-butyl Acetate						
Phenol	57	0.0974 to 0.1196	9,720	690	93	83 to 98
Acetone	1.05	0.0974	38	34.3	10	--
Benzene	61.5	0.0974	169	31	82	--
o-cresol	206	0.0974	2,107	25	99	--
methyl ethyl ketone	4.56	0.0974 to 0.1196	1,215	720	37	36 to 42
Lube Oil Refining Wastewater/Isobutylene						
Phenol	0.7	0.1019	268	209	23	17 & 26
n-butyl acetate	168	0.1019	5,960	13	99.8	99.8 & 99.9
o-cresol	4.8	0.1019	21	215	88	84 & 96
Methyl ethyl ketone	2.49	0.1019	4,190	2,745	35	33 & 36
Lube Oil Refining Wastewater/n-butyl Acetate						
Phenol	57	0.1010 & 0.3042	8,751	90	99	98.8 & 98.8
o-cresol	206	0.1010 & 0.3042	892	5.5	99.4	99.3 & 99.5
Methyl ethyl ketone	4.56	0.1010 & 0.3042	12,216	4,020	67	52 & 82
Ethylene Quench Water/Isobutylene						
Phenol	0.7	0.1010	66.9	63.1	5.7	--
Benzene	487	0.1010	71.1	2.9	95.9	--
Toluene	1,690	0.1010	40.5	2.3	94.3	--
Xylenes	--	0.1010	40.3	1	97	--
Ethylene Quench Water/Isobutane						
Phenol	0.2	0.0973	68.2	66.0	3.2	--
Benzene	338	0.0973	81.2	2.4	97.0	--
Toluene	1,460	0.0973	43.8	1.6	96.3	--
Xylenes	--	0.0973	33.6	1	93	--
Syrene Wastewater/Isobutylene						
Benzene	407	0.1072	290	10	96.6	--
Ethyl benzene	--	0.1072	120	4	96.7	--
Styrene	--	0.1072	15	1	93	--

[a] F_s/F_w = solvent mass flow rate/water mass flow rate
[b] Average values for runs of 2 or more.
[c] Use of & denotes only two values.

Source: Earhart, et al. (1976), Reference 10.

TABLE 7.5.8. CONDITIONS AND RESULTS FOR MINI-PLANT EXTRACTION RUN

Solvent = n-butyl acetate (dispersed phase)

Water flow rate = 9.46 L/h = 9.48 kg/h

Solvent flow rate = 3.56 L/h = 3.18 kg/h

Solvent to water ratio = 0.33 kg/kg = 0.38 L/L

Density of solvent = 0.876 kg/L (25°C)

Shaft rotation speed = 1,200 rpm

Estimated droplet size = 0.75 mm diameter

Column pressure (top) = 390 kPa

Average column temperature = 20.5°C

Rotor disc diameter = 3.81 cm

Stator hole diameter = 5.72 cm

Component	Feed water (ppm)	Steady state raffinate (ppm)	Percent removal
acetic acid	850	785	8
acetaldehyde	300	250	17
2-butanol	180	60	67
methyl isobutyl ketone	130	4	97
acetone	0	1,910	--
n-butyl acetate	0	7,320	--

Source: Reference 11.

7.5.2.3 Results of Other Studies: EPA summaries of solvent extraction data--

Two earlier studies[12,13] were conducted by EPA summarizing available solvent extraction data as shown in Table 7.5.9. These and other related data from the same studies can also be found in Reference 14, the U.S. EPA Treatability Manual.

7.5.3 Cost of Treatment

As noted in EPA's Treatability Manual it is quite difficult to predict costs of solvent extraction because of the wide variety of systems, feed streams, and equipment that may be involved. However, EPA, in Volume IV of the Treatability Manual does present some cost data based on a waste phenol feed of 45,000 lbs/hr containing 1.5 percent phenol by weight and a similar toluene solvent feed rate. (K_D = 2 for the phenol/toluene/water distribution coefficient.) The unit is a rotating disc unit containing an equivalent of about five theoretical stages to produce a wastewater discharge containing 75 ppm phenol. Using the equations provided in Kirk Othmer (Volume 9, Liquid-Liquid extraction), approximately five additional theoretical stages would be required to achieve a discharge level of 21 ppm which is slightly above the design residual phenol level of the entering solvent stream.

The costs are presented in Table 7.5.10 with capital costs modified by ENR index adjustment from 3119 to 4230 (May 1986) and minor changes made in the costs of toluene and power to represent May 1986 values. The annual costs of $917,000/year represent costs in excess of $21 per 1000 gallons of treated wastewater, up from the value of $17 per 1000 gallons provided in Reference 14 (1980 dollars). Assuming capital costs are related to size (number of stages) through a 0.7 exponential factor as indicated in Reference 14, the capital costs shown in Table 7.5.10 would increase from $1.5 to over $2.4 million to achieve a discharge level of 21 ppm phenol in the effluent wastewater (almost $3.0 million if the phenol content of the toluene solvent is assumed to be zero and wastewater phenol discharge level is at 1 ppm). Total annual operating costs would be well in excess of $30/1000 gallons.

TABLE 7.5.9. RESULTS OF SOLVENT EXTRACTION STUDIES

Chemical	Description of study			Results of study	Comments
	Study type[a]	Study type[b]	Influent conc.		
Acrolein	R	U		Extractable w/xylene. Solvent recovery by azeotropic distillation.	
Acrylonitrile	R	U		Extractable w/ethyl ether.	
Chlorobenzene	R	U	600 ppm	3 ppm effluent conc. using chloroform solvent.	
bis-chloroethyl ether	R	U		Extractable w/ethyl ether and benzene.	
Chloroethane	R	U		Extractable w/alcohols and aromatics.	
1,1-Dichloroethane	R	U		Extractable w/alcohols, aromatics and ethers.	
Hexachloroethane	R	U		Extractable w/aromatics, alcohols and ethers.	
1,1,2,2-Tetrachloroethane	R	U		Extractable w/aromatics, alcohols and ethers.	
1,1,1-Trichloroethane	R	U		Extractable w/alcohols and aromatics.	
1,1,2-Trichloroethane	R	U		Extractable w/aromatics, methanol and ethers.	
Dichloroethylene	L,B	I*	49 ppm	Kerosene effluent conc. 2 ppm; C_{10}-C_{12} effluent conc. 1+ ppm.	Solvent extraction w/kerosene & C_{10}-C_{12} hydrocarbon at 7:1 solvent to wastewater ratio.
Ethylene Dichloride	P, C	I*	23-1,804 ppm @ 2.76-3.76 L/min	A 5.5:1 water to solvent ratio gave 94-96% reduction. C_{10}-C_{12} paraffin solvent at 5:1 to 16.5:1 water to solvent ratio showed 94-99% reduction.	Wastewater contained 14 other halocarbons including 30-350 ppm 1,1,2-trichloroethane and 5-197 ppm 1,1,2,2-tetrachloroethane. A 532 L/min extractor w/1,000 ppm influent estimated to have a capital cost of $315,000 and total annual cost of $143,000 including credit for recovered EDC.

[a] Describes the scale of the referenced study:
B - Batch Flow
C - Continuous Flow
L - Laboratory Scale
P - Pilot Scale
R - Literature Review

[b] Describes the type of wastewater used in the referenced study:
I - Industrial Wastewater
U - Unknown

Source: Reference 12
*Reference 13

TABLE 7.5.10. ESTIMATED COSTS FOR A LIQUID-LIQUID EXTRACTION SYSTEM

Operating Characteristics	Value
Water/phenol/feed	45,000 lb/hr containing 1.5% phenol (by wt); temperature is 110°F.
Toluene feed	45,000 lb/hr (containing 20ppm phenol from steam stripper reecycle).
Discharge water	Contains 75 ppm phenol.
Extraction column	Rotating disc type; 6 ft diameter, 60 ft high; made from carbon steel; contains 50 compartments and equivalent of about 5 theoretical stages. (Equilibrium distribution coefficient of phenol between toluene and water is about 2.)
Loss of toluene/cycle	Approximately 0.1%/cycle.
Electrical requirements (column only)	One 10 hp electric motor.
Operation	330 d/yr; 24 hr/d.

Fixed capital costs based on an ENR index of 4,230 (May 1986) are estimated to be $1,500,000 (up from an estimate cost of $1,100,000 provided by reference 14 in 1980). Estimation of annual operating cost is presented below.

Cost item	Annual quantity	Cost per unit quantity	Annual cost[a] $	
Direct operating cost				
Labor				
Operating	12,000 man hr	$16/hr	192,000	
Maintenance			16,000	
				208,000
Chemicals - Toluene	15,000 gal	$1.35		20,300
Materials				16,700
Steam	$33\ 10^6$ lb	$5/1,000 lb		165,000
Power	150,000 kWh	$0.05/kWh		7,500
Total				417,500
Total indirect Operating Cost				500,000
Total annual operating cost[a]				917,500

[a] Excludes annual credit for phenol recovery.

Source: Reference 14 (modified to represent May 1986 dollars).

Conceptual designs and economic analyses were carried out for several cases in the Reference 8 study, including extraction of nitrobenzene with diisobutyl ketone (DIBF - a low boiling solvent); and extraction of acrolein by methyl isobutyl ketone (MIBK), n-butyl acetate, toluene, and 1,1,2,2-tetrachloroethane (all high boiling solvents). The costs derived represent 1982 dollars. The costs, while lower, appear to be in reasonable agreement with the costs of Reference 14, given the differences in base year and operating volumes and concentrations.

Table 7.5.11 presents a breakdown of cost components for extraction of 1,000 ppm of nitrobenzene from 11.4 m^3/h (50 gpm) of water at 30°C using DIBK. Two cases are considered, with and without vacuum steam stripping to recover residual DIBK from the effluent water. There is clearly a substantial incentive to recover DIBK.

Table 7.5.12 summarizes the cost components for extraction of 200 ppm of acrolein from 30,000 lb/hr of water by means of four different high boiling solvents. Details of these analyses are given in Table 7.5.13 for the MIBK solvent systems. Procedures are identical for the other three solvents. The costs range from $8.55 to $13.48 per 1,000 gallons of water, with 1,1,2,2-tetrachloroethane being least expensive because of low steam cost, and toluene the most expensive because of high capital cost. No cost penalty was imposed on the chlorinated hydrocarbon for possible extra processing to ensure full removal from the treated water.

A similar set of analyses was also completed for the extraction of 200 ppm acrylonitrile using methylene chloride and tetrachloroethane as the solvents. Costs per 1000 gallons of water treated were $9.27 and $4.10, respectively. The difference is due to lower steam costs associated with the use of the higher boiling solvent which is not taken overhead during solvent regeneration. Again no penalty was imposed for recovery of solvents from the water phase.

The methods used for the cost calculations for extractions of 2-chlorophenol and nitrobenzene are somewhat different from those used for the cost calculations for the extraction of acrolein and acrylonitrile. These, as noted in Reference 8, cover a range of conditions which might occur in different plant locations.

TABLE 7.5.11. PRELIMINARY EXTRACTION FOR NITROBENZENE EXTRACTION USING DI-ISOBUTYL KETONE (DIBK)

	Case I No Solvent Recovery	Case II Including Steam Stripping
Direct Costs:		
Regenerator	$ 50,700 (41.0%)	$ 50,700 (30.5%)
Extract-Solvent		
Heat Exchanger	27,200 (22.0%)	27,200 (16.4%)
Extractor	22,100 (17.9%)	22,100 (13.3%)
Reboiler	17,500 (14.1%)	17,500 (10.5%)
Regenerator Condenser	6,200 (5.0%)	6,200 (3.7%)
Vacuum Stripper		33,000 (19.9%)
Stripper Condenser		9,400 (5.7%)
Total Direct Cost	$123,700 (100%)	$166,100 (100%)
Indirect Costs:		
(38% of Direct Costs)	$ 47,000	$ 63,100
Fixed Capital Investment (FCI)	$170,700	$229,200
Fixed Charges:		
Depreciation (8% FCI)	$ 13,700/yr	$ 18,300/yr
Maintenance (6% FCI)	10,200	13,800
Insurance and Taxes (3% FCI)	5,100	6,900
Total Fixed Charges (17% FCI)	$ 29,000/yr	$ 39,000/yr
Direct Operating Costs:		
Make-Up Solvent	$ 71,400/yr	$ 9,100/yr
Utilities: 100# Steam		3,100
400# Steam	32,500	32,500
Cooling Water	1,000	2,300
Labor, Supervision, Lab Charges	41,300	41,300
Total Direct Operating	$146,200/yr	$ 88,300/yr
Annual Operating Cost:	$175,200/yr	$127,300/yr

Operating Costs (per 1,000 gallons of wastewater)

Items	Case I No Solvent Recovery	Case II Including Steam Stripping
Labor-dependent	$1.65	$1.65
Capital-dependent	1.16	1.55
Solvent	2.86	0.37
Utilities	1.34	1.52
Total Operating Cost	$7.01	$5.09

Source: Reference 8

TABLE 7.5.12. BREAKDOWN OF OPERATING COSTS FOR EXTRACTION OF ACROLEIN

	Costs - $/1000 Gallons of Water			
Solvent	MIBK	Butyl Acetate	Tetrachloroethane	Toluene
Labor	2.477	2.477	2.477	2.477
Capital	3.054	3.223	3.756	6.347
Solvent loss	1.453	1.446	0.746	0.558
Utilities	4.109	3.747	2.079	4.605
Credit for Acrolein	(-0.511)	(-0.511)	(-0.511)	(0.511)
TOTAL	10.58	10.38	8.55	13.481

Source: Reference 8.

TABLE 7.5.13. ESTIMATION OF OPERATING COST: EXTRACTION OF ACROLEIN BY MIBK (30,000 lb/hr WATER, 200 ppm ACROLEIN)

Item and Basis	Dollars per year	Dollars per 1000 gallon water
Operating Labor Charges:		
1/3 operator/shift at 125,000 dollars/operator/shift	45,000	1.501
Labor Dependent Charges:		
Fringe Benefits 22% of operating labor	9,900	0.331
Supervision, Clerical, 18% of operating labor	8,100	0.270
Operating Supplies, 10% of operating labor	4,500	0.151
Laboratory, 15% of operating labor	6,750	0.225
Fixed Charges:		
Maintenance, 6% of DFC	22,890	0.764
Depreciation, 10% of DFC	38,150	1.273
Insurance, 1% of DFC	3,820	0.127
Local Taxes, 2% of DFC	7,640	0.255
Factory Expenses, 5% of DFC	19,080	0.636
Make-Up Solvent Costs:		
Loss in Regenerator	19,380	0.646
Loss in Stripper	24,190	0.807
Utilties:		
150 psig steam, $\frac{\$\ 8.90}{1000\ \text{lb}}$	84,810	2.829
Cooling water, and refrigeration	38,390	1.280
Credit for by Product Acrolein (1/2 x market price)	(-15,320)	(-0.512)
Total Operating Cost Without Interest	317,260	10.580
Interest, 10% of DFC	38,150	1.272
Total Operating Cost With Interest	355,410	11.854

7.5.4 Overall Status of Process

7.5.4.1 Availability--

Although liquid-liquid extraction processes have not been extensively applied to the treatment of waste streams, they are extensively used within the chemical process industry to affect separations and recoveries. Table 7.5.14 lists a number of processing equipment units which can be used for liquid-liquid extractions. Advantages and disadvantages of each type are listed in the table, and these are discussed in References 1, 9, 14 and other standard texts dealing with separation processes. There are a number of commercial suppliers of liquid-liquid extraction equipment and accessory equipment such as that needed for the regeneration of solvent and removal of solvent from the wastewater effluent.

7.5.4.2 Application--

Integration of equipment into an overall system for successful treatment of waste streams will require considerable analysis of the waste stream of interest and the candidate processes. Liquid-liquid extractions are most useful when separations involve materials that are not easily separated by distillation or other treatment processes. Generally, liquid-liquid extractions of water streams are conducted to remove materials which have high water solubility and therefore almost invariably a low Henry's Law Constant. Air or stream stripping do not appear to be viable options for wastes of this type. Liquid-liquid extractions may be particularly applicable when the relative volatilities of solute/solvent compounds make separation by distillation difficult and high concentration levels make carbon adsorption uneconomical.

Options with regard to choice of solvent and design parameters are many and varied. Although design and operation of a liquid-liquid extraction system to achieve acceptable effluent levels is theoretically possible, existing experimental and field data indicate that most units, as now designed and operated, fall short of this goal.

TABLE 7.5.14. ADVANTAGES AND DISADVANTAGES OF EXTRACTION TYPES

Class of equipment	Advantages	Disadvantages
Mixer-Settlers	Reliable scaleup Good contacting Handles wide flow ratio Low headroom Many stages available	Large holdup High power costs High capital costs Large floor space Interstage pumping may be required
Gravity Columns Spray Column Packed Column Tray Column	Low capital cost Low operating cost Simple construction Handles wide flow ratio (tray column) Handles suspended solids (spray column)	Extensive backmixing (spray, packed column) Limited throughput with small density difference Cannot handle high flow rate (packed column) High headroom Low efficiency (spray column) Difficult scaleup Internals subject to fouling (packed column)
Mechanically Agitated Columns Agitated Column Pulsed Column	Good dispersion Reasonable cost Many stages possible Relatively easy scaleup Handles systems of high interfacial tension	Limited throughput with small density difference Cannot handle emulsifying systems Cannot handle high flow ratio
Centrifugal Extractors	Handles low density difference and high interfacial tension between phases Low holdup Low space requirements Small inventory of solvent Handles stable emulsions	High capital cost High operating cost High maintenance cost Limited number of stages in single unit Subject to fouling

Source: Reference 10, 12-14

7.5.4.3 Environmental Impact--

Properly designed and operated, the liquid-liquid extraction process does not appear to pose significant problems, primarily because both process exit streams contain potential contaminants that must be addressed as part of the process. The solvent will contain solute (contaminant in the feed) that must be removed if the solvent is to function adequately in recycle. The treated waste stream (assuming all significant traces of contaminant have been transferred to the solvent) could in practice contain dissolved solvent which may or may not be significant and warrant additional treatment. Because the potential conditions are recognized and must be dealt with by system designers, the environmental impacts of a viable liquid-liquid extraction system should be minimal.

7.5.4.4 Advantages and Limitations--

Some potential advantages of liquid-liquid extraction processes are:

- Recovery of costly materials can be accomplished usually without threat of thermal decomposition or chemical interaction.
- Recovery (separation) of materials which have similar relative volatilities or adsorption isotherms can generally be accomplished by liquid-liquid extraction.

Some potential limitations of liquid-liquid extraction are:

- Some residues will generally be present in both the raffinate and extract streams, thus, some provision must be made for their removal and subsequent disposal.
- Economics may not be favorable due to deviations from ideal behavior which alter or limit the extent of removal under acceptable design conditions.

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7.6 CARBON ADSORPTION

Adsorption is a widely-used process for the removal of organic contaminants from gas or liquid waste streams. Activated carbon is the most commonly used adsorbent. Largely nonpolar, it is a particularly effective adsorbent for the removal of hydrophobic, high molecular weight organic compounds from aqueous streams. However, it is also a good adsorbent for many of the solvent and other low molecular weight organic compounds considered in this document.[1] Activated carbon adsorption must be considered a potentially viable treatment technology for many solvent bearing waste streams, either as a primary treatment for moderately high (up to 0.5 percent) concentrations of organic compounds in an aqueous stream or as a secondary polishing type treatment for much lower levels of contamination.[1,2] The cost effectiveness of adsorption is dependent on flow rates and concentrations of the organic contaminants and on the adsorptive capacity of the carbon for the contaminants. Adsorption should be cost effective for concentrations of organic compounds up to about 1,000 mg/L, and could be cost effective for concentrations up to 5,000 mg/L. Most likely for concentrations above 5,000 mg/L, another unit process may be more effective.[3]

Activated carbon is available as a powder (PAC) or in the form of granules (GAC). GAC is most commonly used because its larger size is most amenable to handling in the equipment used to achieve contact and regeneration.[4] Both types of carbon adsorbent have large surface areas, far in excess of their nominal external surface areas. Surface areas, resulting from a network of internal pores 20 to 100 angstroms in diameter, are of the order of 500 to 1,500 square meters per gram. Porosities can be as large as 80 percent. The characteristics of the micropore structure are largely dependent on the activation process which is a controlled process of dehydration, carbonization, and oxidation of raw materials including coal, wood, peat, shell, bone, and petroleum based residues. The capacity of an activated carbon for a contaminant is a function of the surface area and the surface binding process and can approach one gram per gram of carbon.

Adsorbent binding forces result from the interaction of the surface molecules with the field of force of the surface atoms. The attractive forces, in the case of activated carbon, are generally weaker and less specific than those of chemical bonds and, hence, the term physical adsorption is used to describe the binding mechanism. In agreement with the nature of the forces, the effective range of their forces is small, and the adsorbed material is generally present only as a monolayer upon the adsorbent surface. The process is considered analagous to condensation of gas molecules, or to crystallization from a liquid. The process is reversible, and molecules held at the surface will subsequently return to the fluid stream with the length of time elapsing between adsorption and desorption dependent upon the intensity of the surface forces. Adsorption is a direct result of this time lag.

Water solubility and carbon affinity are two properties that, in general, correlate with the adsorption of hazardous contaminants onto activated carbon. Generally, less soluble organic materials are better adsorbed. Several factors are associated with decreased water solubility of organics and, as a result, correlate with increased adsorption: high molecular weight, low polarity, low ionic character, low pH for organic acids or high pH for inorganic bases, and aromatic structures. As a rule of thumb, molecules of higher molecular weights are attracted more strongly to activated carbon than are molecules of lower molecular weights. Strongly ionized or highly polar compounds are more water soluble and thus usually poorly adsorbed.[5] Compounds with solubilities of less than 0.1 g/mL in water and molecular weights between 100 to 1,000 are considered moderately to highly adsorbable.[1]

Several other aspects of molecular structure also affect adsorbability. In general, branch-chain compounds are more adsorbable than straight-chain compounds. Increasing hydrocarbon unsaturation also tends to decrease solubility and increase carbon adsorption. Thus, unsaturated organics such as ethylenes tend to more readily adsorb on carbon than saturated compounds, such as ethanes. Table 7.6.1 identifies the specific waste characteristics that affect adsorption; Table 7.6.2 summarizes the influence of substituent chemical groups on adsorbability.

The adsorption of organic compounds by adsorbents is usually determined in the laboratory through adsorption isotherm tests. These tests measure, at a given temperature, the amount of substance adsorbed and its concentration in the surrounding solution at equilibrium. Isotherms provide information on the relative affinity of an organic compound for the adsorbent and the adsorption

TABLE 7.6.1. WASTE CHARACTERISTICS THAT AFFECT ADSORPTION BY ACTIVATED CARBON

A. General

  1. Polar, low-molecular weight solvents and ignitables with high degrees of solubility are poorly adsorbed.

  2. Conversely, nonpolar, high-molecular weight solvents and ignitables with limited solubility tend to be preferentially adsorbed.

B. Molecular Structure

  1. Branched-chain compounds are more adsorbable than straight-chain compounds.

  2. Type and location of substituent groups also affect the degree to which a compound may be adsorbed from solution. Table 7.6.2 gives some general guidelines as to how substituent groups affect adsorbability.

C. Effect of pH

  1. The affect of pH on carbon solute equilibrium varies significantly from compound to compound. Adsorption isotherms for some solvents and ignitables are affected dramatically, whereas others show no significant change as a function of pH.

  2. Dissolved organics generally adsorb most efficiently at that pH which imparts the least polarity to the molecule. For example, a weak solvent can be expected to adsorb best at low pH value.

D. Temperature Effects

  1. Adsorption reactions are generally exothermic; therefore lower temperatures favor adsorption. Although this makes physical sense, little information has been found that documents significant shifts in adsorbability within the range of temperatures normally encountered in waste stream applications.

E. Physical Form

  1. Carbon adsorption is suitable for aqueous wastes, nonaqueous liquids and gases.

  2. The oil and grease concentration should be less than 10 mg/L.

  3. Suspended solids concentrations higher than about 10-70 mg/L will cause clogging of the bed.

TABLE 7.6.2. INFLUENCE OF SUBSTITUENT GROUPS ON ADSORBABILITY

Substituent	Nature of influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater; many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic is more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double bonds	Variable effect as with carbonyl.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability
Aromatic rings	Greatly increase adsorbability.

Source: Reference 6

capacity. Thus, isotherm tests can be useful in making qualitative evaluations of different carbons for adsorption of specific components from a given waste stream.

Isotherms data are frequently evaluated using the Freundlich Equation, which describes the adsorbability characteristics of a constituent for a given carbon. This equation can be expressed as follows:

$$\frac{x}{m} = kC_f^{1/n} \qquad (1)$$

where: x = mass of adsorbate, mg

m = mass of dry adsorbent, g

k = constant, adsorbability indicator

C_f = solution concentration at equilibrium, mg/L

$1/n$ = constant, adsorption intensity

Values of k and 1/n for a compound are found by a plot of experimentally determined carbon adsorption data in which values of x/M are plotted against C on log-log paper.

The k intercept is an indicator of adsorption capacity, and the slope 1/n an indication of the change in capacity with concentration. A high k value and a low 1/n value would be representative of a high capacity adsorption system that is not strongly dependent upon contaminant concentration.

The adsorption data are useful in estimating the relative effectiveness of an adsorbent for organic compounds. However, care must be exercised in assessing performance when the waste stream contains a large number of competing contaminants. Although it is possible to develop equilibrium equations that apply to multi-component systems as noted in standard texts on adsorption and Perry's Chemical Engineers' Handbook, most users will rely on laboratory scale carbon adsorption/isotherm tests to assess performance and design an appropriate system for a specific waste stream.

The constants k and 1/n are summarized in Table 7.6.3. These have been ranked in decreasing order of their k value as determined by isotherm tests using Filtrasorb 300 activated carbon. Table 7.6.4 shows similar data for activated carbon adsorption using 5 grams of Westvaco WVG carbon per liter of solution.

TABLE 7.6.3. CARBON ADSORPTION ISOTHERM DATA

	k	1/n
Solvents of Concern		
1,2-dichlorobenzene	129	0.43
chlorobenzene	91	0.99
p-xylene	85	0.19
nitrobenzene	68	0.43
ethylbenzene	53	0.79
tetrachloroethylene	50.8	0.56
methyl ethyl ketone	36	0.211
trichloroethylene	28.0	0.62
toluene	26.1	0.44
carbon tetrachloride	11.1	0.83
cyclohexanone	6.2	0.75
trichlorofluoromethane	5.6	0.24
n-butyl alcohol (butanol)	5.5	0.50
1,1,1-trichloroethane	2.48	0.34
ethyl acetate	2.4	0.78
methylene chloride	1.3	1.16
Other Compounds		
acrolein	1.2	0.65
benzene	1.79	0.53
bromoform	19.6	0.52
1,1,2,2-tetrachloroethane	10.6	0.37
1,3-dichloropropene	8.21	0.46
1,2-dichloropropane	5.86	0.60
1,1,2-trichloroethane	5.81	0.60
1,1-dichloroethene	4.91	0.54
1,2-dichloromethane	3.6	0.8
chloroform	1.0	1.6
ethylidene dichloride (1,1-dichloroethane)	1.79	0.53
hexachloroethane	96.5	0.38

Sources: References 7 and 8.

*Data for Adsorbent Filtersorb 300

TABLE 7.6.4. ADSORPTION OF SOLVENTS AND OTHER ORGANICS BY ACTIVATED CARBON

Compound	Molecular weight	Aqueous solubility weight %	Concentration (mg/liter)		Adsorbability	
			Initial	Final	g of compound/ g of carbon	Reduction (%)
Solvents of Concern						
Methanol	32.0	α	1,000	964	0.007	3.6
Butanol	74.1	7.7	1,000	466	0.107	53.4
Isobutanol	74.1	8.5	1,000	581	0.084	41.9
Pyridine	79.1	α	1,000	527	0.095	47.3
Toluene	92.1	0.047	317	66	0.050	79.2
Ethyl benzene	106.2	0.02	115	18	0.019	84.3
Nitrobenzene	123.1	0.19	1,023	44	0.196	95.6
Ethyl acetate	88.1	8.7	1,000	495	0.100	50.5
Acetone	58.1	α	1,000	782	0.043	21.8
Methyl ethyl ketone	72.1	26.8	1,000	532	0.094	46.8
Methyl idobutyl ketone	100.2	1.9	1,000	152	0.169	84.8
Cyclohexanone	98.2	2.5	1,000	332	0.134	66.8
Other Solvents						
Benzene	78.1	0.07	416	21	0.080	95.0
Aniline	93.1	3.4	1,000	251	0.150	74.9
Propylene glycol	76.1	α	1,000	884	0.024	11.6
Ethylene dichloride	99.0	0.81	1,000	189	0.163	81.1
Ignitables						
Allyl alcohol	58.1	α	1,010	789	0.024	21.9
Formaldehyde	30.0	α	1,000	908	0.018	9.2
Acetaldehyde	44.1	α	1,000	881	0.022	11.9
Acrolein	56.1	20.6	1,000	694	0.061	30.6
Paraldehyde	132.2	10.5	1,000	261	0.148	73.9
Ethylenediamine	60.1	α	1,000	706	0.062	29.4
Ethyl acrylate	100.1	2.0	1,015	226	0.157	77.7
Acrylic acid	72.1	α	1,000	355	0.129	64.5

Source: Reference 9.

Test Conditions: 5 g of Westvaco WVG Carbon Per Liter of Solution.

7.6.1 Process Description

A schematic of a carbon adsorption system utilizing a prefilter and a multiple hearth furnace regeneration system is shown in Figure 7.6.1. In this system, adsorbed material is driven from the carbon surface by thermal forces; however, other methods (e.g., extraction or steam stripping) can be used to drive off adsorbed material held largely by physical rather than chemical forces. Regeneration is usually complete, although some loss of effective surface area over time (3 to 8 percent per cycle)[2] can result from build up of hard to remove adsorbent, attrition, and other mechanisms. Collection or destruction of the desorbed material will also be necessary for these regeneration processes.

Carbon adsorption is applicable to single-phase aqueous solutions containing low concentration of organic contaminant (up to 0.5 weight percent)[3] and inorganic contaminants (up to 0.1 weight percent).[5] It is also applicable to some organic liquid solutions (e.g., those consisting of a poorly adsorbed solvent and a readily adsorbed solute), although it is less likely that the selectivity will approach that for adsorption from a water stream.

Carbon adsorption may be used as a pretreatment process for conventional biological treatment, but is more frequently used as a polishing step for biological treatment effluent to remove compounds that are resistant to biodegradation. In this capacity, it is generally used for high volume waste streams which contain dilute organic constituents.

7.6.1.1 Pretreatment Requirements--

Pretreatment of the feed to carbon adsorption columns is often required to improve performance and/or prevent operational problems. As discussed in Reference 10, there are four primary areas where pretreatment requirements for different waste forms and characteristics may be required. These include:

1. Equilization of flow and concentrations of primary waste constituents.
2. Filtration.

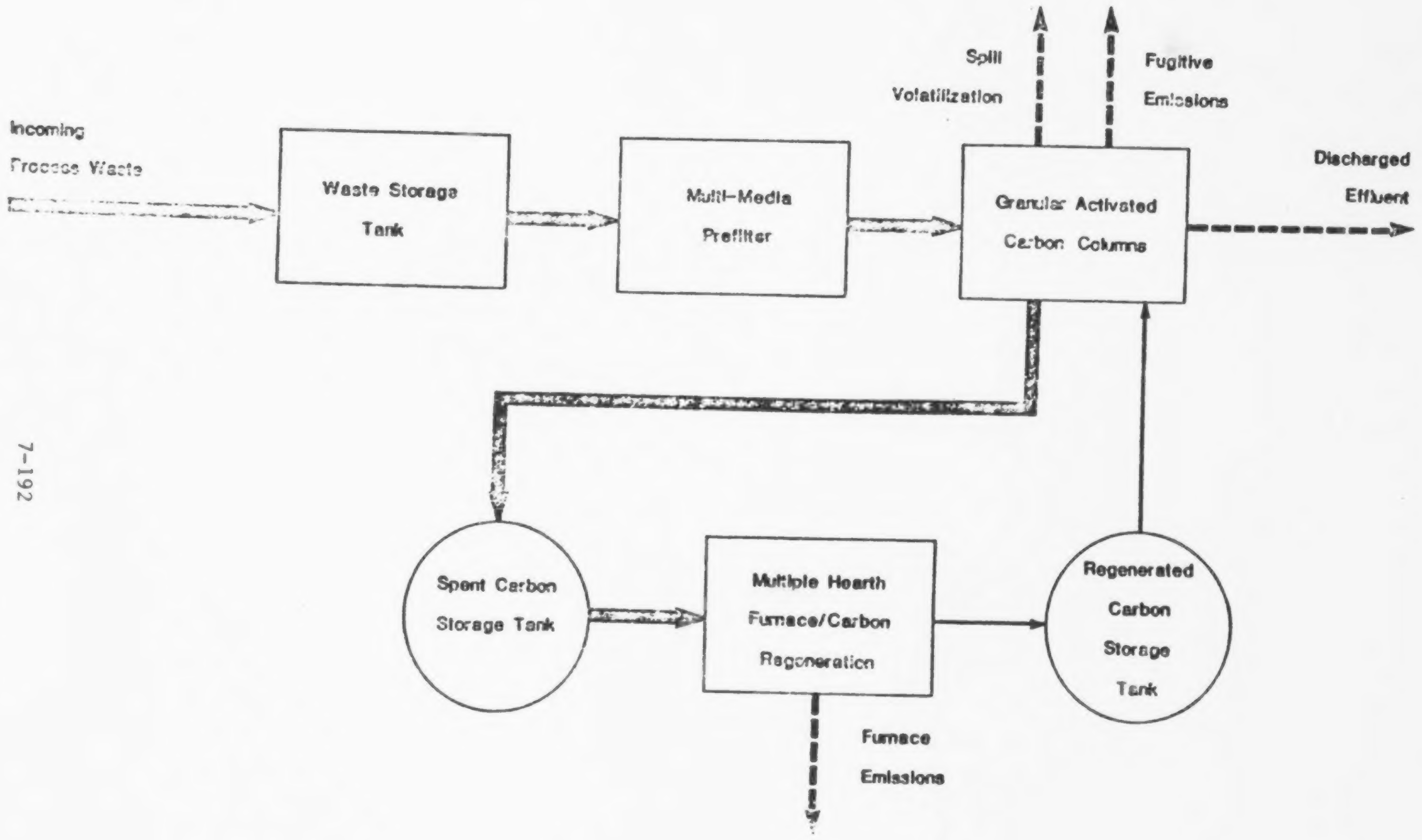

Figure 7.6.1. Carbon adsorption flow diagram.

Source: Reference 4.

3. Adjustment of pH.

4. Adjustment of temperature.

Equalization of flow and concentrations of primary waste constituents--It is generally assumed that both the flow to the GAC columns and the concentration of the primary waste constituent, namely a solvent or ignitable in the feed, are constant. Such is not generally the case, and since variations in either flow or concentration can have a detrimental impact on system performance, it is necessary to make provisions to equalize flow and minimize concentration surges.

Flow equalization is accomplished by employing a surge tank of sufficient capacity to accommodate flow variations. The result is a constant flow rate to the GAC columns. Concentration equalization can be handled in the same manner as flow equalization by employing surge tanks. However, provisions must be made for mixing tank contents prior to discharging to the GAC columns. Mixing prevents concentration surges which can lead to premature column leakage and breakthrough or conversely, low concentration swings resulting in premature regeneration of an underloaded GAC column.

Filtration--It is a general requirement for GAC processes that the feed of the column be low in suspended solids. In treating solvent and ignitable waste streams, it has been suggested that solids greater than 50 mg/L in concentration will interfere with column operation.[1] It is difficult, however, to set an upper limit on the absolute level of suspended solids that is acceptable. This is because the physical nature of the solids is as important as their concentration. For example, finely divided, silty solids tend to pass through the bed, but coarse material of varying particle size could rapidly form a mat on top of the bed, constricting flow.

In addition to solids removal, many waste contaminants can interfere with carbon adsorption of solvent and ignitable waste streams. For example, if calcium or magnesium are present in concentrations greater than 500 mg/L, these constituents may precipitate out and plug or foul the column.[5] Oil and grease in excess of 10 mg/L can interfere in column operation.[1] Lead and mercury are also of concern because they may compete for adsorption sites and are difficult to remove from the carbon during the regeneration cycle.[11] The presence of many other compounds can influence adsorption as they compete for available adsorption sites on the carbon surface.

For efficient use of GAC for treating solvent waste streams, removal of suspended solids and other waste contaminants noted above must be achieved by pretreatment with, for example, multi-media pressure filters. Such filters are very compatible with fixed bed adsorption processes and can be readily integrated into a total design. Other possibilities include membrane filtration when a highly clarified feed is desired; ultrafiltration if high molecular weight contaminants were encountered (over 1,000); and reverse osmosis could be used to concentrate a feed containing numerous dissolved species both organic and inorganic. Obviously other pretreatments will be needed to remove dissolved solids such as calcium and magnesium.

Adjustment of pH--GAC adsorption systems are sensitive to changes in pH. If the contaminants to be removed are either weakly acidic or weakly basic, then the pH of the feed will effect their adsorption. Weakly acidic organics such as cresols or cyclohexanone are most readily adsorbed in the nonionized state and consequently a low pH (acid) favors adsorption. Weakly basic compounds such as aniline or dimethylamine are also most readily adsorbed in their nonionized state and, therefore, adsorption is favored by high pH (alkaline). The adsorption of neutral organic compounds is unaffected by pH.

The control of the feed pH should perhaps be considered a subcategory of the previously discussed concentration/equalization requirement. It can be readily controlled by applying pH measurement and feedback control for acid or base addition to the equalization system at the surge tank to achieve the desired pH feed to the GAC adsorption columns.

Adjustment of Temperature--The adjustment of temperature is rarely required in GAC adsorption for solvent and ignitable processes. High feed temperature could lead to increased VOC emissions to air in an open gravity feed system and is unfavorable for adsorption and retention of the volatile constituents. If the possibility for temperature surges exists, temperature moderation through flow equalization should be considered.

7.6.1.2 Operating Parameters--

Process design activities must take into account a number of equipment design parameters to develop a system which is optimal for the characteristics of the waste or wastes to be treated. The design parameters will be considered in terms of both the adsorption system and the regeneration or desorption system.

Adsorption System--Isotherms, determined in a laboratory, measure the affinity of activated carbon for the "target" adsorbates in the process liquid. This provides data for determining the amount of carbon which will be required to treat the full scale process stream. Carbon requirements will be based on a limiting constituent for which attainment of effluent limitations is the most difficult. However, adsorption isotherms can vary widely for different carbons, and isotherm data cannot be used interchangeably.

Table 7.6.5 gives properties of some commercially available granulated activated carbons. Properties of a typical powdered activated carbon are shown in Table 7.6.6. Adsorption properties of the two types of carbon are generally comparable. The principal difference is in the particle size; the fine size of the PAC makes it unsuitable for use in the contacting and regeneration equipment used for GAC applications.

A typical continuous adsorption system consists of multiple columns filled with activated carbon and arranged in either parallel or series. Total carbon depth of the system must accommodate the "adsorption wavefront"; i.e., the carbon depth must be sufficient to purify a solution to required specifications after equilibrium has been established. Bed depths of 8-40 feet are common. Minimum recommended height-to-diameter ratio of a column is 2:1. Ratios greater than 2:1 will improve removal efficiency but result in increased pressure drop for the same flow rate. Optimum flow rate must be determined in the laboratory for the specific design and carbon used. For most applications, 0.5 to 5 gpm per square foot of carbon is common.

Various configurations are available for GAC adsorption applications. Based on influent characteristics, flow rate, size and type of carbon, effluent criteria and economics, each design offers uniqueness in its mode of operation. Figure 7.6.2 illustrates several arrangements typically used for GAC adsorption systems. There are two basic modes of operation for column

TABLE 7.6.5. PROPERTIES OF SEVERAL COMMERCIALLY AVAILABLE CARBONS

	ICI America Hydrodarco (lignite)	Calgon Filtrasorb 300 (bituminous)	Westvaco Nuchar WV-L (bituminous)	Witco 517 (12x30) (bituminous)
PHYSICAL PROPERTIES				
Surface area, m^2/g (BET)	600 - 650	950 - 1050	1000	1050
Apparent density, g/cm^3	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/g^3	22	26	26	30
Real density, g/cm^3	2.0	2.1	2.1	2.1
Particle density, g/cm^3	1.4 - 1.5	1.3 - 1.4	1.4	0.92
Effective size, mm	0.8 - 0.9	0.8 - 0.9	0.85 - 1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cm^3/g	0.95	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5 - 1.7	1.5 - 1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)[a]				
Larger than No. 8 (max. %)	8	8	8	--
Larger than No. 12 (max. %)	--	--	--	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	--	--	--	--
Iodine No.	650	900	950	1000
Abrasion No. minimum	b	70	70	85
Ash (%)	b	8	7.5	0.5
Moisture as packed (max. %)	b	2	2	1

---

[a] Other sizes of carbon are available on request from the manufacturers.

[b] No available data from the manufacturer.

-- Not applicable to this size carbon.

TYPICAL PROPERTIES OF 8 X 30-MESH CARBONS

	Lignite carbon	Bituminous coal carbon
Total surface area, m^2/g	600 - 650	950 - 1,050
Iodine number, min	500	950
Bulk density, lb/ft^3 backwashed and drained	22	26
Particle density wetted in water, g/cm^3	1.3 - 1.4	1.3 - 1.4
Pore volume, cm^3/g	1.0	0.85
Effective size, mm	0.75 - 0.90	0.8 - 0.9
Uniformity coefficient	1.9 or less	1.9 or less
Mean particle dia., mm	1.5	1.6
Pittsburgh abrasion number	50 - 60	70 - 80
Moisture as packed, max.	9%	2%
Molasses RE (Relative efficiency)	100 - 120	40 - 60
Ash	12 - 18%	5 - 8%
Mean-pore radius	33 A	14 A

Source: Reference 9

TABLE 7.6.6. TYPICAL PROPERTIES OF POWDERED ACTIVATED CARBON (PETROLEUM BASE)

Surface Area m^2/g(BET)		2,300 - 2,600
Iodine No.		2,700 - 3,300
Methylene Blue Adsorption (mg/g)		400 - 600
Phenol No.		10 - 12
Total Organic Carbon Index (TOCI)		400 - 800
Pore Distribution (Radius Angstrom)		15 - 60
Average Pore Size (Radius Angstrom)		20 - 30
Cumulative Pore Volume (cm^3/g)		0.1 - 0.4
Bulk Density (g/cm^3)		0.27 - 0.32
Particle Size	Passes: 100 mesh (wt%)	97 - 100
	200 mesh (wt%)	93 - 98
	325 mesh (wt%)	85 - 95
Ash (wt%)		1.5
Water Solubles (wt%)		1.0
pH of Carbon		8-9

Source: Reference 6.

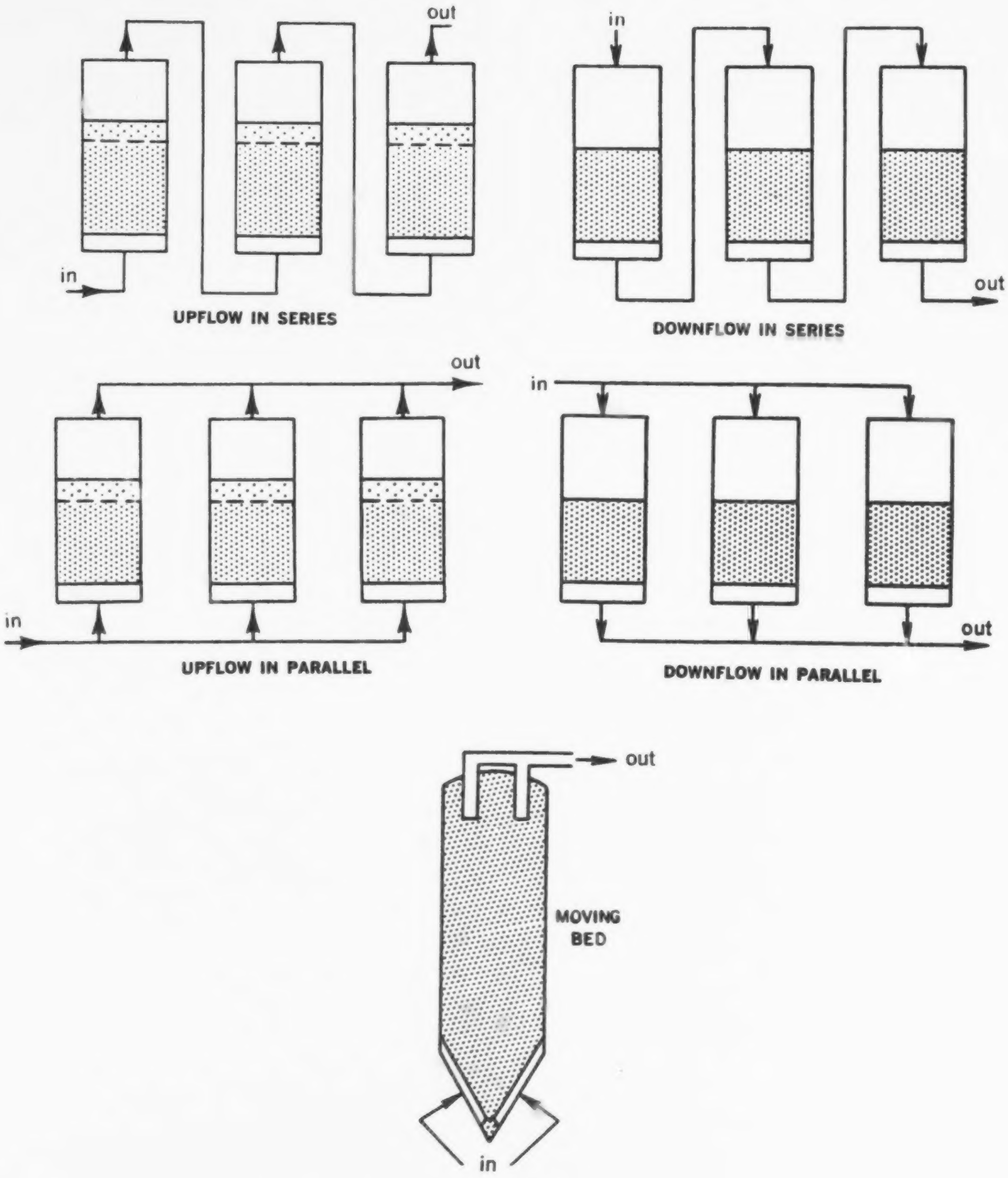

Figure 7.6.2. CARBON BED CONFIGURATIONS

Source: Reference 12.

adsorbers; namely, fixed beds and moving or pulsed beds. In the fixed bed mode, the entire bed is removed from service when the carbon is to be reactivated. In the moving or pulsed bed, only the exhausted (inlet) portion of the total bed is removed as an increment of new adsorbent is added simultaneously.

Arrangement in series permits the first column to become saturated with impurities while a solution of required purity is obtained from the final column. At this point, the first column is emptied and refilled with fresh carbon or regenerated. Fluid flow is redirected so that the column is now placed in the downstream position, affording a form of countercurrent use of the carbon.

The adsorption beds of both series and parallel design can be operated in either an upflow or downflow direction. A downflow mode of operation must be used where the GAC is relied upon to perform the dual role of adsorption and filtration. Although lower capital costs can be realized by eliminating pretreatment filters, more efficient and frequent backwashing of the adsorbers is required. Application rates of 2-10 gallons per minute per square foot (gpm/ft^2) are employed, and backwash rates of 12-20 gpm/ft^2 are required to achieve bed expansions of 20-50 percent. The use of a supplemental air scour can be used to increase efficiency of the backwashing.

In the upflow-expanded mode, while prefiltration is normally required to prevent blinding the beds with solids, smaller particle sizes of GAC can be employed to increase adsorption rate and decrease adsorber size. Application rates can be increased in the upflow-expanded mode even to the extent that the adsorbent may be in an expanded condition.[10]

The design arrangements offer the following advantages and limitations noted in Reference 12.

Method	Comments
Adsorbers in Parallel	- For high volume applications - Can handle higher than average suspended solids (<65-70 ppm) if downflow - Relatively low capital costs - Effluents from several columns blended, therefore, less suitable where effluent limitations are low

Method	Comments
Adsorbers in Series	- Large volume systems - Easy to monitor breakthrough at tap between units - Effluent concentrations relatively low - Can handle higher than average suspended solids (<65-70 ppm) if downflow - Capital costs higher than for parallel systems
Moving Bed	- Countercurrent carbon use (most efficient use of carbon) - Suspended solids must be low (<10 ppm) - Best for smaller volume systems - Capital and operating costs relatively high - Can use such beds in parallel or series
Upflow-expanded	- Can handle high suspended solids (they are allowed to pass through) - High flows in bed (~15 gpm/ft^2)

The above systems are not generally used with the much finer powdered activated carbons. The PAC systems now used involve mixing the PAC with the waste stream to form a slurry which usually can be separated later by methods such as filtration or sedimentation. PAC is generally used with biological treatment to enhance organic removal by biological processes.[13]

Regeneration--The success of an economical adsorption system usually depends on the regenerability of the adsorbent. The exception is where there are very long adsorption or loading cycles due to very low concentrations of solvent constituents in the inlet feed; this type of system usually operates on a "throw away" basis". If very large quantities of adsorbent are involved, then regeneration and reuse are required. The regeneration techniques employed in industry are thermal regeneration, steam regeneration, and acid or base regeneration[10]. Solvent washing or biological treatment are other methods that are occassionally used for regeneration. The most commonly applied regeneration technique for GAC systems is thermal.

Thermal regeneration involves high temperatures and a controlled gaseous atmosphere. The regeneration of the spent carbon can be considered to take place in three distinct phases. First, wet carbon is dried at a temperature range of approximately 100-150°C. Water and some low boiling organics will be removed during this process but higher boiling solvents such as nitrobenzene (b.p. 210.8°C), cresols (b.p. 201.9°C), and 1,2-dichlorobenzene (b.p. 173°C) will remain. Next, the temperature is raised to 250 to 750°C where these more tightly bonded solvents and higher boiling organics are removed by vaporization. An inert gas atmosphere can be employed to minimize oxidation. Finally, the temperature is raised to 800 to 975°C where residues and tars that may have accumulated are reacted and driven off the carbon surface. Steam is sometimes used to assist removal. Even with careful control, GAC losses are reported to be 3 to 8 percent per cycle due to both oxidation and mechanical attrition. Regeneration furnaces have been designed to conduct all three steps of drying, vaporization under inert gases, and regeneration separately in different zones. Multiple hearth furnaces and fluidized-bed furnaces are two types of thermal regenerators commonly found in commercial use.

Steam regeneration can be used to displace the liquid in the adsorber bed, heat up the adsorbent and, finally, strip off the solvents and ignitables from the GAC. The solvents and the other low molecular weight organics of concern are volatile enough to permit regeneration with steam. Average pressures of one to three atmospheres are utilized with steam flow rates of 1/2 to 4 $lbs/min/ft^3$. The amount of steam required depends upon the size of the carbon bed. The majority of steam used in regeneration is used to heat the carbon bed to the necessary temperature for vaporization to occur. The heat capacities of the adsorbed constituents and their heats of vaporization do not represent a large fraction of the total steam requirement. Thus units for steam usage should be in lb steam/lb carbon or equivalent.

As discussed in the pretreatment section, the adsorption of weak organic acids and bases from aqueous solutions is very dependent upon pH. Therefore, if the adsorbed organic is acidic, regeneration with a basic solution is feasible. Conversely, basic constituents can be regenerated with an acidic solution. Acid or base regeneration is not as widely used as other regeneration techniques, but nonetheless, some solvents such as cresols and ethylene diamine have been successfully recovered commercially, by base and acid regeneration, respectively.

7.6.1.3 Post-Treatment Requirements--

Air and water discharges from carbon adsorption systems employing carbon regeneration can be relatively innocuous. Under proper design and operating conditions, the treated water will generally be suitable for discharge to surface waters. Other aqueous streams such as backwash, carbon wash and transport waters are recycled or sent to a settling basin. Emissions will result from thermal reactivation, but when afterburners and scrubbers are used, the controlled emissions are essentially non-polluting. In some installations, particulates must be removed from the air stream (e.g., via a cyclone and baghouse) resulting in a solid waste.[1]

7.6.1.4 Treatment Combinations--

The high cost associated with the treatment of moderate to high total organic carbon (TOC) wastes and the ineffectiveness of carbon as an adsorbent for many low molecular weight water soluble organic compounds has impacted the use of carbon adsorption as a waste treatment technology. Except when used alone as a polishing step for low levels of adsorbable materials in aqueous streams, carbon adsorption is usually employed in a "treatment train" with other treatment processes to achieve maximum efficiency at reduced cost.

The following treatment train combinations illustrate the use of activated carbon systems with other technologies to optimize performance. The process trains shown do not represent the only possible configurations. They do, however, represent the treatment technologies which, when combined with activated carbon, are expected to have broadest range of applicability and effectiveness. These also have been demonstrated to some degree for treatment of hazardous aqueous solvent and other organic containing waste streams. The examples have been taken from material presented in Reference 14 and in other material cited herein.

Treatment Train One

Figure 7.6.3 illustrates a sequence of solids removal and biological treatment followed by granular carbon adsorption for polishing of the liquid effluent. This train is applicable to treatment of wastewaters high in TOC and low in toxic (to a biomass) organics.

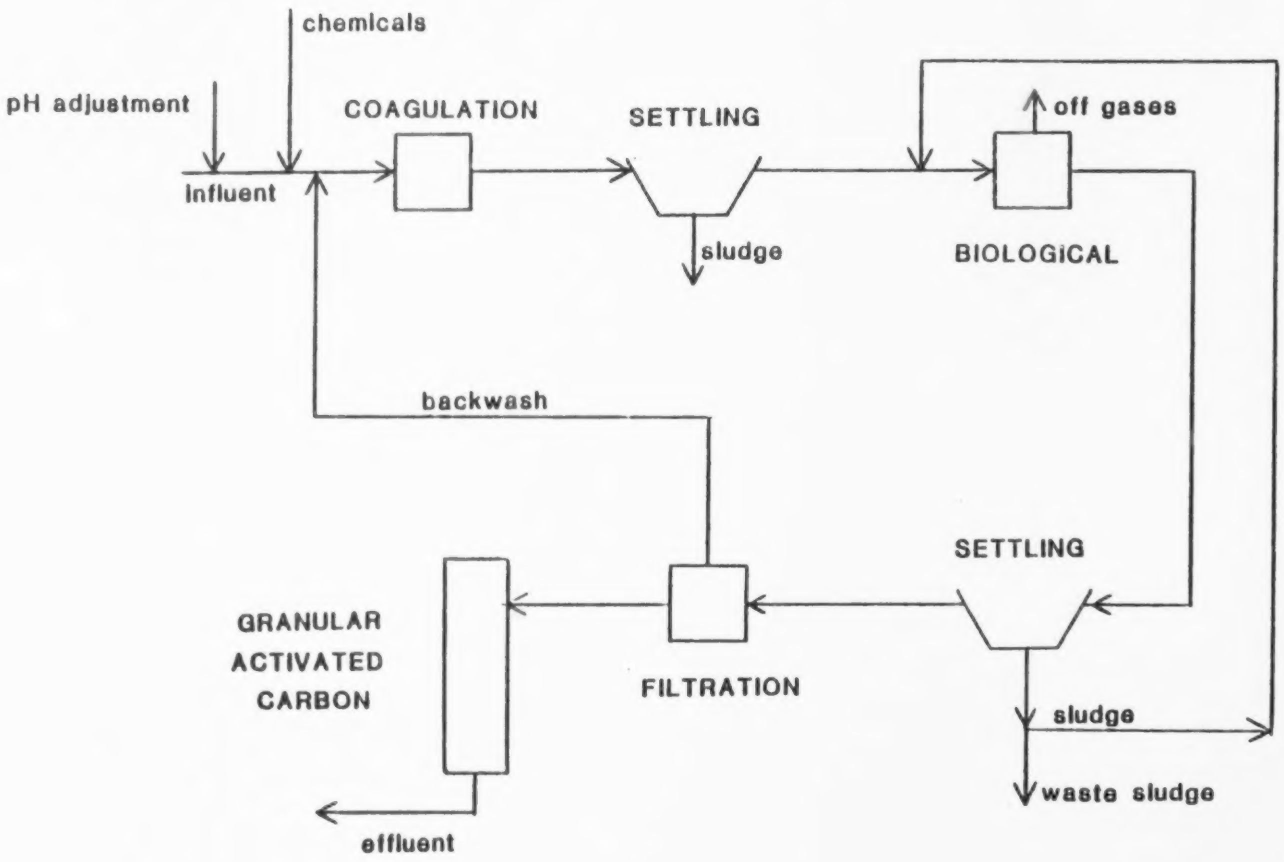

Figure 7.6.3. Schematic of biological/carbon adsorption treatment train.

Source: Reference 14.

Biological treatment such as activated sludge, rotating biological contactors, or anaerobic filters are used to reduce BOD as well as biodegradable toxic organics. This reduces the organics load to subsequent treatment (adsorption) processes. To prevent rapid head losses caused by accumulation of solids in the adsorption columns, clarification and multi-media filtration are provided following biological treatment to reduce suspended solids to 25-50 mg/L. Granular carbon adsorption is then used to polish liquid effluents to remove nonbiodegradable and toxic organics.

This process train is expected to be highly cost effective. Its success, however, is dependent on biological system performance. Moreover, the presence of high concentration of volatile organic constituents may create a potential air contamination problem during biodegradation. Three by-product wastes are produced: chemical sludge, biological sludge, and spent carbon. Spent carbon can be regenerated but the sludges must be subjected to further treatment prior to disposal.

Because the process is intended to handle multi-component waste streams, pollutant recovery for reuse is unlikely. The only potential for such recovery is during carbon regeneration if materials can be desorbed by steam or solvent washing. This would be reasonable only if a small number of separable compounds were sorbed on the carbon.

Treatment Train 2

The flowsheet depicted in Figure 7.6.4 employs the same unit processes as in Figure 7.6.3, but granular carbon is positioned ahead of the biological treatment system. This process train, which also is applicable to high TOC wastewaters, is used when highly adsorbable waste stream components may be toxic to biological cultures. The rationale is to utilize the activated carbon to protect the biological system from toxicity problems. Therefore, the carbon is allowed to pass relatively high concentrations of biologically nontoxic organics and selectively adsorb only those constituents which impact negatively on the subsequent biological process. The train is appropriate only for wastes with appropriate chemical configuration and adsorption characteristics and may be impractical for many wastes.

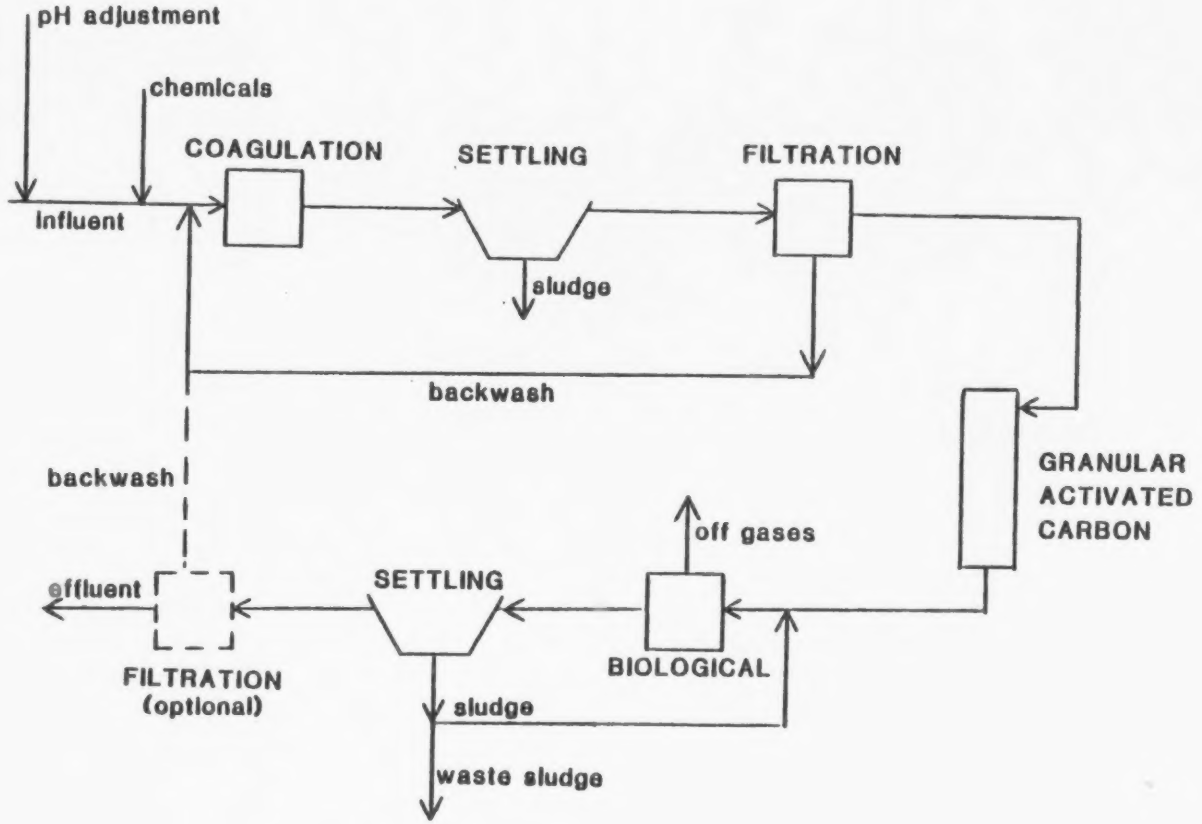

Figure 7.6.4. Schematic of carbon adsorption/biological treatment train.

Source: Reference 14.

In this configuration, the chemical coagulation step (including settling and filtration) plays a role both in soluble inorganics removal and in particulate removal to minimize head losses in GAC columns. As with the treatment train above there is little potential for recovery of pollutants.

Treatment Train 3

The third process train, illustrated in Figure 7.6.5, utilizes biophysical treatment which is a combination of biological and powdered activated carbon treatments (PACT^{TM}) conducted simultaneously. This approach is simpler than the previously described sequential carbon-biological treatments and has the potential of achieving comparable effluent quality. Potential advantages include the use of less costly powdered carbon and minimization of the physical facilities required. Spent carbon-biological sludge can be regenerated or dewatered and disposed directly. However, if the latter approach is considered, it is necessary to include additional costs for raw carbon purchase and disposal of toxics-laden carbon when making economic comparisons. Further information concerning the use of PAC can be found in other references, including References 14 and 15.

Treatment Train 4

A processing system consisting of a stripping unit and a carbon adsorption system is illustrated in Figure 7.6.6. This configuration will be applicable primarily to organic wastewaters, although provision for chemical coagulation and removal of inorganics is provided. This treatment train is suited to situations involving volatile and nonbiodegradable toxic organics. It is especially pertinent if a single or limited number of volatile compounds are present which can be recovered from the overhead condensate stream (if steam stripping is used).

Aside from pH adjustment prior to stripping, little pretreatment is necessary, other than filtration to remove solids to prevent the build-up in the column stripping unit.

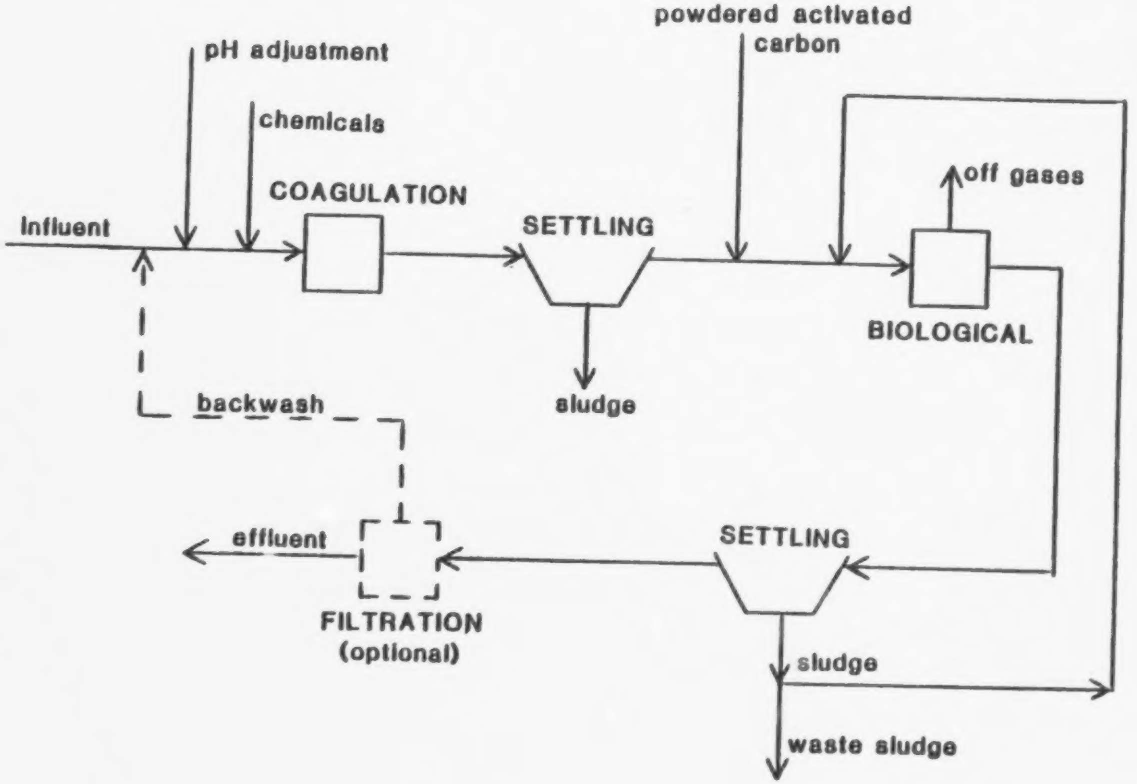

Figure 7.6.5. Schematic of biophysical treatment train.

Source: Reference 14.

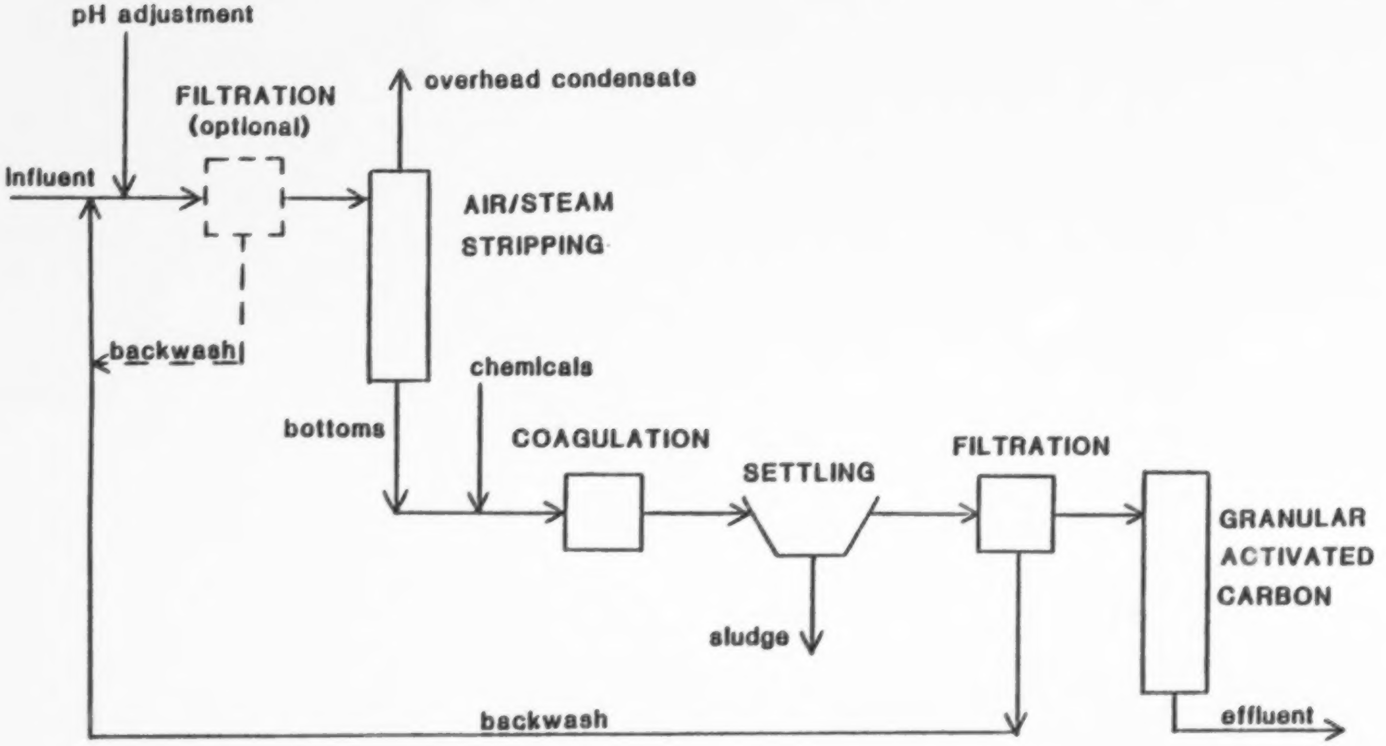

Figure 7.6.6. Schematic of stripping/carbon adsorption treatment train.

Source: Reference 14.

In addition to carbon treatment effluent, this process train generates three waste streams: overhead condensate, chemical sludge, and spent carbon. Assuming that carbon will be regenerated, either onsite or by a commercial service, the two remaining streams require additional treatment and/or disposal. Preferably, the organic phase of the overhead condensate can be recovered and reused, with the water phase returned to the treatment system. However, if this is not possible, incineration is the best method for condensate disposal. Chemical sludge should be dewatered and disposed by a method commensurate with the materials contained in the sludge.

7.6.2 Demonstrated Performance

Information gathered from activated-carbon manufacturers and industry indicates that many granular-activated carbon systems are being used for the treatment of hazardous aqueous solvent and ignitable bearing wastes and wastewaters. One EPA study[6], performed in 1982, found that over 100 GAC systems were being used nationally to treat industrial wastewaters. Another report[13] documented the use of PAC at seven and four facilities in the United States and Japan, respectively.

Despite the large number of units in use, data for full scale applications are incomplete for two primary reasons. For many applications, essential operating parameters or pollutant removal characteristics have not been generated or are considered to be proprietary information. The available information does, however, contain material gathered from a wide variety of data sources, including carbon manufacturers, industrial users of activated carbon, the available literature, and EPA files.

A major shortcoming of the available data base dealing with the removal of solvents and other low molecular weight organics from aqueous waste streams by activated carbon, is the sparsity of performance data for the higher concentration (>0.1 percent) levels. In addition, most of the data found in the literature do not consider the removal of individual compounds from concentrated waste streams, although data for BOD, COD, TOC, and other parameters are fairly common. Data for individual compounds provided in EPA's background document for solvents (Reference 5) are, with few exceptions, for treatment of influent concentrations at the part per billion level. All data presented, however, do indicate that levels acceptable for direct discharge can be reached for essentially all solvents of concern. Thus, the utility of adsorption as a treatment process hinges on the economics of the specific situation.

Data taken from References 6 and 8 have been summarized in Tables 7.6.7 and 7.6.8. These data provide results of bench/pilot and full scale GAC systems, respectively. Because of the sparsity of information concerning system design and operating conditions, including carbon loading, no attempt has been made to include such information in the tables. However, more details can be found in the cited references, e.g., Reference 8.

Data are similarly sparse for systems using PAC, although PAC and GAC should exhibit little, if any, difference in adsorption performance. As noted previously, the most significant difference between the two sorbents is in their particle size. The fine particle size of PAC is not suitable for use in contacting equipment normally used for GAC systems.

The addition of powdered activated carbon to the aeration basin of a biological activated sludge system combines physical adsorption with biological oxidation and assimilation. It has been shown to be particularly effective in treating waste streams which are variable in concentration and composition. The characteristic advantages of the addition of PAC over conventional activated sludge are:

1. Higher BOD and COD removal.
2. Stability of operation with variability in influent concentration and composition.
3. Enhanced removal of toxic substances and priority pollutants.[15]

A performance summary for a full scale study is shown in Table 7.6.9. In this study PAC was added to the sludge and the mixture was then fed to three activated sludge units operating in parallel. This was followed by two clarifiers also operating in parallel. The sludge from the clarifiers was sent to a multiple hearth furnace for carbon reactivation. The influent

TABLE 7.6.7. DATA REPORTED FROM BENCH SCALE AND PILOT PLANT GAC SYSTEMS

Constituent	Concentration (mg/L) Influent	Concentration (mg/L) Effluent	Removal (%)	Reference
Acetone	60	6	90	6
Chloroform	34	0	100	6
	11	ND	>99	8
	92	ND	>99	8
	12	ND	>99	8
1,1-dichloroethane	59	4	93	6
	40	0	100	6
	26	ND	>99	8
	91	ND	>99	8
	64	9	86	8
1,2-dichloroethane	2,000	12	99.4	6
	1,000	190	81	6
	450	0	100	6
	510	ND	>99	8
	1,120	150	87	8
	1,220	330	73	8
1,2-dichlorpropane	16	0	100	6
	28	ND	>99	8
	7	ND	>99	8
Ethanol	1,440	140	90	6
1,1,1,trichloroethane	5	ND	>99	8
	12	ND	>99	8

TABLE 7.6.8. DATA REPORTED FROM FULL SCALE GAC SYSTEMS

Constituent	Concentration (mg/L) Influent	Concentration (mg/L) Effluent	Removal (%)	Reference
Acetone	10	1	90	6
Benzene	10	1	90	6
	590	210	64	6
	590	210	64	6
Carbon tetrachloride	4.3	1.8	58	6
Chloroform	190.	136	29	6
	70	18	74	8
Cresol	16.5	0.6	96.2	6
	5,000	350	93	6
1,1-dichloroethylene	130	ND	99	8
Methylene chloride	108	28	73	6
	38	3	92	8
	32	--	78	8
Tetrachloroethylene	100	32	68	8
Toluene	--	--	99.7	6
	2,500	630	75	6
	--	--	99	6
	2,500	630	75	6
Trichloroethylene	12	5	58	8
	2,000	4.4	99	8
Trichloroethane	2,500	1.9	99	8

TABLE 7.6.9. DATA REPORTED FROM FULL SCALE PAC SYSTEM

Constituent	Concentration (mg/L) Influent	Effluent	Percent removal
Benzene	0.105	0.0009	99
Carbon tetrachloride	0.094	0.0014	99
Chlorobenzene	1.720	0.030	98
Chloroform	0.201	0.021	89
1,2-dichlorobenzene	0.259	0.120	54
Ethylbenzene	0.041	0.0017	96
Methyl chloride	1.770	ND	>99
Nitrobenzene	0.454	ND	>99
Tetrachloroethylene	0.024	0.0017	93
Toluene	0.519	0.0047	99
1,1,1-trichloroethane	0.013	0.0006	95
Trichloroethylene	0.041	0.0019	95
Trichlorofluoromethane	0.155	0.0030	98
BOD	169	5.3	97
COD	596	10.9	98

Source: Reference 6. IT Enviroscience

System Operating Parameters:

Flow rate: 151,372 m^3/d
Carbon Dosage: 134 ppm
Aerator Detention Time: 8.4 hrs
Sludge Age: 38 days
Regeneration Technique: Multiple Hearth

concentrations were low because this study was from a contaminated municipal wastewater treatment system; however, the results are promising, showing the high removal possible with the combination of PAC and activated sludge.

7.6.3 Cost of Carbon Absorption

The cost of carbon adsorption treatment can be described in terms of capital investment, and operation and maintenance costs. Capital costs consist of direct and indirect expenses. For the small scale system, direct capital investment costs include the purchase of a waste storage tank, a prefilter, carbon columns, a waste feed pump, piping and installation. For the large scale system, direct capital investment costs include the purchase of the components in the small scale system plus storage tanks for spent and regenerated carbon, a multiple hearth furnace and automatic controls.[16]

A model has been developed by ICF, Inc. (Reference 17) for calculating carbon adsorption costs. Table 7.6.10 contains the equations used in this model to calculate direct capital costs as a function of carbon consumption rate and storage volume. Indirect capital costs include the costs of engineering, construction, contractor's fee, startup expenses, spare parts inventory, interest during construction, contingency and working capital. These costs are expressed as percentages of either direct capital costs or the sum of direct and indirect capital costs as summarized in Table 7.6.11. Direct and indirect capital costs are assumed to be incurred in year zero.

Operation and maintenance costs also consist of direct and indirect costs. Direct operation and maintenance costs (in 1984 dollars) include the operating labor and electricity and carbon consumption. Table 7.6.10 also contains the equations used in the model to calculate direct operation and maintenance costs. As with the capital costs, the model considers operation and maintenance costs for carbon consumption rates less and greater than 400 lbs/day. For large scale systems, the operation and maintenance costs also include the natural gas consumption necessary for the furnace. Indirect operation and maintenance costs include the costs for insurance and the system overhead.

TABLE 7.6.10. DIRECT COSTS FOR CARBON ADSORPTION[a]

Carbon Consumption Rate (lbs/day)	Direct Capital Costs ($)	Direct Operation and Maintenance Cost[b] ($/yr)
less than 400	$1{,}256(c)^{.603} + 140(s)^{.54}$	$29(c)^{.6} + 350(c)(cp) + 619(c)^{.168}(h) + 5(c)(p)$
greater than 400	$14{,}231(c)^{.522} + 140(s)^{.54}$	$58(c)^{.657} + 35(c)(cp) +$ $105(c)^{.455}(h) +$ $25{,}012^{.383}(c)(p) +$ $1.49\ 10^{6}(c)(f)$

where: c = carbon consumption rate in pounds per day

s = storage volume in gallons

cp = carbon price in dollars per pound ($0.8/lb)

h = hourly wage rate in dollars per hour ($14.56/hr)

p = power price in dollars per kilowatt-hour ($0.05/KWh)

f = fuel price (natural gas) in dollars per Btu ($$6\text{x}10^{-6}$/Btu)

[a] Cost estimates were developed for three model treatment systems (three small scale and three large scale systems). The cost estimates for these systems were then used to develop a cost equation in the form of a power curve.

[b] The power requirement is derived from the equipment specifications.

SOURCE: Reference 17

TABLE 7.6.11. INDIRECT COSTS FOR CARBON ADSORPTION

Item	Percent of direct capital costs	Percent of the sum of direct and indirect capital costs	Percent of total annual cost[a]
Indirect Capital Costs			
Engineering and Supervision	12	0	0
Construction and Field Expenses	10	0	0
Contractors Fee	7	0	0
Startup Expenses	5	0	0
Spare Parts Inventory	2	0	0
Interest During Construction	10	0	0
Contingency	0	15	0
Working Capital	0	18	0
Indirect Operation and Maintenance Costs			
Insurance, Taxes, General Administration	0	5	0
System Overhead	0	5	10

[a] The total annual cost is defined as the sum of the total capital cost multiplied by the capital recovery factor and the total operation and maintenance costs.

Based on the RCRA Risk-Cost Analysis Model, Table 7.6.12 shows carbon adsorption costs for 100, 400, 1,000 and 2,500 gal/hr processes.

7.6.4 Overall Status of Process

7.6.4.1 Availability--

Activated carbon adsorption is a widely used technology for treating waste streams containing organic compounds, including many hazardous organic solvents and other low molecular weight organic compounds. Its ability to treat solvents and other organics has been demonstrated at bench, pilot, and full scale levels by many firms. Manufacturers of activated carbon produce a carbon to fit just about any service need. Companies who use these activated carbon systems, both GAC and PAC, are numerous and may be found in several literature sources (see References 6, 8, 14, and 18). Equipment designers and suppliers can be found in the Chemical Engineering Equipment Buyers' Guide published by McGraw-Hill, New York, NY.

7.6.4.2 Application--

Activated carbon adsorption systems are widely used in industry to process chemical product streams as well as waste streams. The technology has proven to be effective as a pretreatment for aqueous wastes prior to their introduction into biological treatment systems. Concurrent treatment of waste streams with PAC and biological treatment has also proven to be effective. However, the most common application of carbon adsorption systems would appear to be as a polishing step for low concentration level effluents from other treatment technologies. The use of carbon adsorption systems for treatment of wastes containing 0.5 percent or greater organic concentration levels is not considered to be cost effective. Other technologies should be considered at these concentrations.

Removal efficiencies which permit direct discharge can usually be met by GAC systems for most organic solvents and other low molecular weight organics. However, performance will depend upon the specifics of waste stream contamination, including the need for pretreatment, post-treatment, and other aspects of system operation.

TABLE 7.6.12. CARBON ADSORPTION COSTS[a]

	Quantity processed (gal/hr)			
	100	400	1,000	2,500
Capital Expenditures				
Capital Cost Including Installation[b] ($1,000)	59	561	904	1,462
Annual Operation and Maintenance ($1,000)[c]				
Energy	2	11	27	68
Labor	23	35	53	80
Carbon	7[e]	27	67	168
Other	1	5	10	18
Capital Recovery	10	99	160	259
Total Annual Cost	42[e]	177	317	593
Cost per 1,000 gal[d]	210[e]	221	159	119

[a] Costs are based on the RCRA RISK-COST ANALYSIS MODEL.[17]

[b] Capital costs for the 100 gal/hr system include waste storage tank, prefilter, carbon columns, waste feed pump, piping and installation; the other flow levels (400, 1,000, 2,500) include these units plus storage tanks for spent and regenerated carbon, a multiple hearth furnace and automatic controls.

[c] These costs are based on the following data:

carbon price = $0.8/lb
hourly wage rage = $14.56/hr
power price = $0.05/kwh
fuel price (natural gas) = $6 x 10^{-6}/Btu
capital recovery factor = 0.177

[d] Unit costs are based on 2000 hours of operation per year.

[e] Modified to reflect a direct relationship between carbon requirement and quantity processed.

*Note: 1984 dollars, prices are similar to 1986 values.

Although the adsorbability of a contaminant/carbon combination does not provide all the information needed to assess the potential applicability of activated carbon to a specific waste stream, it is the prime determinant. Table 7.6.13 illustrates a treatability rating system for priority pollutants based on carbon adsorptability. The table shows that polar, low molecular weight solvent and ignitables with high solubilities (e.g., methylene chloride) are poorly adsorbed on carbon. Conversely, nonpolar, high molecular weight solvents and ignitables with low solubilities (generally less than 0.1 g/mL; e.g., chlorobenzene) were found to be preferentially adsorbed. Data such as that shown in Table 7.6.13 obtained from isotherms, manufacturers' literature, and existing data make it possible to predict performance with some degree of accuracy for compounds of interest provided the characteristics of the stream can be determined and variations are not extreme.

7.6.4.3 Environmental Impacts--

Environmental impacts can result from emissions during the regeneration of carbon. However, there will be no serious environmental impacts if the exit gases are treated by a control system, e.g., an afterburner and/or scrubber, and in some cases, a particulate filter. Where the carbon is chemically regenerated (acid, base, or solvent), the regeneration stream will require future treatment, e.g. incineration or distillation to remove the organic contaminants.

The recovery or reuse of desorbed solutes from the adsorption process is an area where opportunities could exist for both cost savings and reduction of environmental impacts. Disposal of desorbed solutes as waste materials can be costly and also result in an environmental hazard. Therefore,recycling of solute following desorption and recovery should be considered and practiced if possible.

TABLE 7.6.13. REMOVAL RATINGS FOR ORGANIC COMPOUNDS

Compound	Removal rating	Compound	Removal rating
PRIORITY SOLVENTS			
acetone	P	methyl ethyl ketone	G
butanol	G	methyl isobutyl ketone	F
carbon disulfide	G	methylene chloride	P
carbon tetrachloride	G	nitrobenzene	E
chloropenzene	E	pyridine	E
cresols	E	tetrachloroethylene	E
cyclohexanone	G	toluene	G
1,2-dichlorobenzene	E	1,1,1-trichloroethane	G
ethyl acetate	F	trichloroethene	F
ethyl ether	P	trichloromonofluoromethane	G
ethylbenzene	G		
isobutyl alcohol	P	1,1,2-trichloro-1,2,2-trifluoroethane	G
methanol	P	xylene	E
OTHER SOLVENTS			
acetonitrile	F	2-ethoxy ethanol	P
aniline	E	ethyl carbonate	G
benzene	F	ethylene dichloride	G
bis(chloromethyl)ether	G	ethylidene dichloride	F
bromoform	E	furan	F
chloroform	P	furfural	G
cyclohexane	F	hexachloroethane	E
m-dichlorobenzene	E	2-nitropropane	F
dichlorodifluoromethane	F	2-picoline	E
1,1-dichloroethylene	P	propylene glycol	F
1,2-dichloroethylene	F	1,1,1,2-tetrachloroethane	E
1,2-dichloropropane	G	1,1,2,2-tetrachloroethane	E
1,3-dichloropropane	G	tetrahydrofuran	F
1,4-dichloro-2-butene	F	1,1,2-trichloroethane	G
1,4-dioxane	P		
IGNITABLES			
acrolein	P	ethylmethacrylate	P
acrylic acid	F	formaldehyde	P
allyl alcohol	P	glycidylaldehyde	F
allyl chloride	P	methacrylonitrile	P
2,2-bioxirane	F	2-methylaziridine	P
chloracetaldehyde	F	methyl bromide	P
chloromethyl methyl ether	F	1-methylbutadiene	P
chloroprene	F	methyl chloride	P
cumene	E	methyl chlorocarbonate	P
dimethylamine	P	methyl iscyanate	P
dipropylamine	F	methyl methacrylate	P
epichlorohydrin	P	oxirane	G
ethanol	P	paraldehyde	F
ethyl acrylate	F	propylamine	P
ethylenediamine	P	thiomethanol	P
ethylencmine	P		

Source: Reference 3.

Key: E = Excellent Removal - Adsorbs at levels >100 mg/g carbon at C_f = 10 mg/L
Adsorbs at levels >100 mg/g carbon at C_f <1.0 mg/L

G = Good Removal - Adsorbs at levels >100 mg/g carbon at C_f = 10 mg/L
Adsorbs at levels <100 mg/g carbon at C_f <1.0 mg/L

F = Fair Removal - Adsorbs at levels <100 mg/g carbon at C_f = 10 mg/L
Adsorbs at levels <100 mg/g carbon at C_f <1.0 mg/L

P = Poor Removal - C_f = Final concentration of pollutant at equilibrium

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7.7 RESIN ADSORPTION

Resin adsorption is an alternative treatment technology for the removal of organic contaminants from aqueous waste streams. The underlying principle of operation is similar to that for carbon adsorption; organic molecules contacting the resin surface are held on the surface by physical forces and subsequently removed during the resin regeneration cycle. Resin adsorbents can be made from a variety of monomeric compounds which differ in their polarity and thus, their affinity for different types of compounds. The choice of resin type, in combination with modifications in pore structure, can lead to an adsorbent tailored specifically for effective removal of special classes of compounds, e.g., low molecular weight, polar organics. For example, hydrophobic resins such as those prepared from styrene - divinyl benzene monomers, are most effective for nonpolar organics and bonding is largely the result of Van der Waal's forces; acrylic based resins on the other hand are more polar and dipole-dipole interactions may play the major role in the binding of polar molecules to the resin surface. The general concept is that like molecules attract. Polar resins will attract polar organics; nonpolar compounds will be attracted by the more hydrophobic or nonpolar resins.[1]

A significant aspect of resin adsorption is that the attractive forces are usually weaker than those encountered in granulated activated carbon (GAC) adsorption . Regeneration can be accomplished by simple, nondestructive means such as solvent washing, thus providing the potential for solute recovery. Thermal regeneration (generally not possible with resin adsorbents because of their temperature sensitivity) is usually required for carbon adsorbents eliminating the possibility of solute recovery. The resins differ in many respects from activated carbon adsorbents. In addition to differences in the ease and usual methods of regeneration associated with the chemical nature of the two adsorbents, there are significant differences in shape, size, porosity and surface area. Resin adsorbents are generally spherical in shape rather than granular, and are smaller in size and lower in porosity and surface area than GAC adsorbents. Surface areas for resins are generally in the range of 100-700 m^2/g, as opposed to 800-1,200 m^2/g for activated carbon.[1]

Adsorptive capacities are thus less for the resin adsorbents, although the chemical nature and the pore structure of the resin can be tailored to enhance the selectivity of the resin and, therefore, its adsorption capacity for specific organic components.

Properties of several typical resin adsorbents are shown in Table 7.7.1. A more detailed list of physical properties is provided in Table 7.7.2 for a specialty resin provided for experimental study by Rohm and Haas Company, Ambersorb XE-340. The resin was designed initially by Rohm and Haas for the selective adsorption of chloroform. Selectivity was based on controlled pore structure adjustment. Macropores are adjusted such that low molecular weight organics (e.g., chloroform), can rapidly diffuse into the interior of the resin (micropores) for adsorption, but high molecular weight compounds and collodial or bacterial matter are inhibited. The size of the pores protects the active sites from exposure to other materials that would normally be competitive for adsorption and would, thus, reduce the selectivity of adsorption and possibly complicate solute recovery.[2] Selectivity based on chemical structures and pore dimensions is not totally exclusive, however. Ambersorb XE-340, for example, although originally tailored for the adsorption of chloroform, is also a good adsorbent for most other low molecular weight organics, e.g., carbon tetrachloride and trichloroethylene.[2]

Other notable properties of resin adsorbents include their nondusting characteristics, their low ash content, and their resistance to bacterial growth. The last characteristic is primarily a result of the fine pore structure which inhibits bacterial intrusion.[3]

Another significant difference between resin and carbon adsorbents is their cost. Resin adsorbents are much more expensive. They generally will not be competitive with carbon for the treatment of waste streams containing a number of contaminants with no recovery value. However, resin adsorption should be considered if material recovery is practical, selectivity is possible, and for cases where carbon regeneration is not effective. Like carbon adsorption systems, resin adsorption can produce an effluent with low levels of contaminant concentrations, particularly in cases where contaminants are well characterized and few in number. Resin adsorption combined with carbon adsorption may be effective for certain waste streams containing a number of contaminants.[1]

TABLE 7.7.1. PHYSICAL PROPERTIES OF ADSORBENTS

Manufacturer	Adsorbent	Chemical nature	Pore volume (cm^3/g)	Surface area (m^2/g)	Pore diameter average (Å)	Surface polarity
Rohm and Haas	Amberlite XAD-2	Polystyrene	0.68	300	100	Low
	Amberlite XAD-4	Polystyrene	0.96	725	50	Low
	Amberlite XAD-7	Acrylic Ester	0.97	450	85	Intermediate
	Amberlite XAD-8	Acrylic Ester	0.82	160	150	Intermediate
	Ambersorb XE-347	Polymer Carbon	0.41	350	200, 15[a]	Low
	Ambersorb XE-348	Polymer Carbon	0.58	500	200, 15[a]	Intermediate
Mitsubishi	Diaion HP-10	Polystyrene	0.64	500	b	Low
	Diaion HP-20	Polystyrene	1.16	720	70	Low
	Diaion HP-30	Polystyrene	0.87	570	b	Low

[a] Average pore diameter of the macropores and micropores, respectively.

[b] Average pore diameter not available.

Source: Reference 2.

TABLE 7.7.2. TYPICAL PHYSICAL PROPERTIES OF AMBERSORB XE-340

Appearance	Black, spherical, nondusting polymer carbon
Total surface area (N_2, BET method), m^2/g	400
Bulk density, lb/ft^3	37
Bulk density, g/cm^3	0.60
Particle density, g/cm^3 (Hg displacement)	0.92
Skeletal density, g/cm^3 (He displacement)	1.34
Pore volume, cm^3/g	0.34
Particle size (U.S. Sieve Series)	20-50
Crush strength, kg/particle	3.0
Ash content, percent	0.5
Macropore diameter, A	100-350
Micropore diameter, A	6-40
Surface polarity	Very low

Source: Reference 2.

7.7.1 Process Description

Resin adsorption systems are designed and operated in similar fashion to GAC systems. A principal difference will be in the regeneration step; regeneration of the resin is usually performed in situ with aqueous solutions or solvents. Solute recovery from the regeneration liquor will also be required, with distillation the most likely method.

7.7.1.1 Pretreatment Requirements--

Polymeric adsorbents require pretreatment of feed streams to remove suspended solids, oils and greases, and to adjust pH and temperatures, as appropriate. Suspended solids in the influent should be less than 50 mg/L and, in the case of oil and grease, less than 10 mg/L to prevent clogging of the resin bed.[1] The control of pH may be necessary to prevent resin attack and to enhance adsorbability. Low temperature will also generally enhance adsorption. Resin adsorbents, although generally resistant to chemical attack because of their cross-linked structure, should not be brought into contact with compounds such as chemical oxidants and functional reagents which may degrade the resin or poison adsorption sites. High levels of dissolved solids, particularly inorganic salts, do not compete with organics for adsorption sites, and their presence may in some instances increase the adsorption of organics.

Pretreatment options are similar to those proposed previously for carbon adsorption systems. For example, filtration or coagulation/sedimentation type separations can be used for suspended solids, and flotation/extraction procedures can be used for removal of oils and greases. Each pretreatment option will result in a residual which may or may not require additional processing prior to disposal.

There are no definite limitations on the upper or lower contaminant concentration levels that can be treated. An upper limit of 8 percent (for phenol) is suggested in Reference 1, however, to maintain cycle time and regeneration frequency within reasonable limits. As with carbon adsorption, the efficiency of resin adsorption (weight of adsorbed material per weight of adsorbent) is greater at high concentrations.

7.7.1.2 Operating Parameters--

The design of a resin adsorption system requires the development of basic information such as feed stream flow rate, contaminant concentration, and adsorbent type and capacity. Other information such as flow rate variations, suspended solid level, pH, and temperature will be required to ensure that adequate pretreatment precautions and operating practices are followed.

The choice of adsorbent type can be guided by the concept that attractive forces will be greatest for similar molecules. The similarity concept is also useful in identifying regeneration solvents. The solubility of the adsorbate in the regeneration solvent is quite important. The solvent not only must be capable of overcoming the attractive forces of adsorbate/adsorbent but must also remove the adsorbate in the smallest possible volume.

Although the relative strengths of the attractive forces between solute, solvent, and resin can be predicted through the use of solubility parameters,[4] there is no practical method for determining the actual capacity of an adsorbent for contaminants, particularly those existing in complex waste streams. It is, therefore, necessary to carry out experimental studies to determine working capacities for candidate adsorbents. In most cases it will be possible to design systems to achieve EPA treatment standard levels, although it may not be possible for complex mixtures without use of multiple adsorbents (or technologies). Costs may also be prohibitive, and activated carbon may often be a more attractive adsorbent, particularly where solute recovery is not desirable or practical.

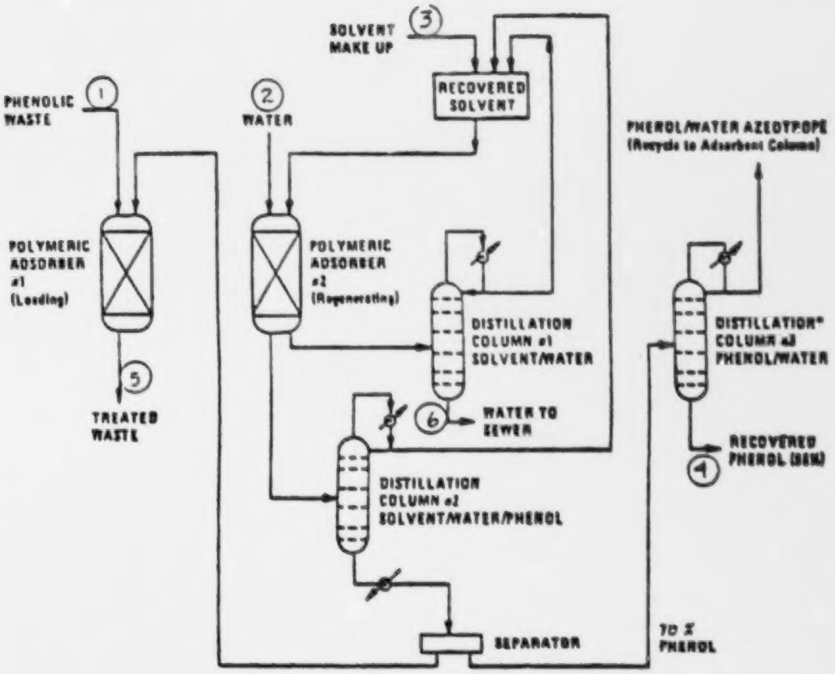
Assuming a resin adsorbent can be found that can achieve required treatment levels, additional tests will be required to identify and select a regeneration process. The selection of a regeneration solvent can be guided by use of solubility parameters. However, other factors such as cost of solvent regeneration and adsorbate recovery must be considered. Distillation appears to be the most likely solvent and solute recovery technology assuming a solvent/solute match can be found that is amenable to such a separation process.

Design of a resin adsorption process operation would include the following steps as a general procedure: 1) determine wastewater effluent purity desired, 2) select adsorbent and determine adsorption capacity, 3) select regeneration process based on bench or pilot scale tests, 4) size adsorbent bed, 5) check loading run length and determine if it is compatible with the regeneration time cycle, 6) repeat 4 and 5 until loading and regeneration cycles are compatible, 7) determine bed dimensions by hydraulic considerations, 8) design and size pumps, storage tanks, pretreatment equipment and auxiliary equipment.[5]

As noted in Reference 1, a system for treating low volume waste streams will commonly consist of two beds. One bed will be on stream while the second is being regenerated as shown in Figure 7.7.1.

The adsorption bed is usually fed downflow at flow rates in the range of 0.25 to 2 gpm per cubic foot of resin; this is equivalent to 2-16 bed volumes/hr, and thus contact times are in the range of 3-30 minutes. Linear flow rates are in the range of 1-10 gpm/ft^2. Adsorption is stopped when the bed is fully loaded and/or the concentration in the effluent rises above a certain level. As noted in the previous section on carbon adsorption, a contact time of 30 minutes may not be adequate for attainment of treatment standards. EPA has suggested that limited contact times may play an important role in reducing column loadings in the field to values less than those predicted from isotherm testing.[6] Reference was made to a study which attributed carbon contact times of greater than 230 minutes to applications which requires high degree of pollutant removal. Although rapid adsorption kinetics are attributed to resin adsorbents, caution should be exercised in assessing the contacting time requirements and design and operating features needed to meet EPA treatment standard concentration levels.

Regeneration of the resin bed is performed in situ with basic, acidic, and salt solutions or recoverable nonaqueous solvents being most commonly used. Basic solutions may be used for the removal of weakly acidic solutes and acidic solutions for the removal of weakly basic solutes; hot water or steam could be used for volatile solutes; and methanol and acetone are often used for the removal of nonionic organic solutes. A prerinse and/or a postrinse with water will be required in some cases to remove certain contaminants such as salts. As a rule, about three bed volumes of regenerant will be required for resin regeneration; as little as one-and-a-half bed volumes may suffice in certain applications.[1]


SOLVENT MAKE UP
③
RECOVERED SOLVENT
PHENOLIC WASTE
①
②
WATER
PHENOL/WATER AZEOTROPE
(Recycle to Adsorbent Column)
POLYMERIC ADSORBER #1 (Loading)
POLYMERIC ADSORBER #2 (Regenerating)
DISTILLATION COLUMN #1 SOLVENT/WATER
DISTILLATION* COLUMN #3 PHENOL/WATER
⑤
TREATED WASTE
⑥
WATER TO SEWER
RECOVERED PHENOL (99%)
④
DISTILLATION COLUMN #2 SOLVENT/WATER/PHENOL
SEPARATOR
70 % PHENOL

Column #3 utilized when highly pure phenol is required.

Material Balance, lbs/hr

	①	②	③	④	⑤ + ⑥
Phenol	264			264	< 10 ppm
Water	21,736	1480		9	23,207
Acetone			4		4
Total	22,000	1480	4	273	23,211

Figure 7.7.1. Phenol removal and recovery system - solvent regeneration of Amberlite adsorbent.

Source: Reference 1.

The use of steam as the regenerating agent should be considered; steam regeneration for volatile organics may provide some cost benefits in that it can reduce the need for subsequent treatment to separate the waste solvent from the dissolved organics. However, the condensed steam may also require additional treatment prior to discharge to also eliminate dissolved organics.

When using steam regeneration for polymeric adsorbents, one must consider the upper temperature limit of the resin in choosing the steam pressure. The styrene based polymeric adsorbents are usually stable to 200°C; acrylic based resins up to 150°C. Since the adsorbed solvent and other organic constituents can cause the adsorbent resin matrix to swell and weaken, removal of these constituents by steaming could result in disruption and breakup of the resin matrix. Therefore, adsorbent stability is of concern when using steam regeneration and should be studied using multi-cycling tests to confirm the integrity of the adsorbent before proceeding with design of the regeneration system.

Steam requirements are normally significantly lower for the polymeric adsorbents than those for granular activated carbon to achieve a certain desorption level of a given constituent. The reason for this is that the attractive forces binding the solvent or other organic constituent to the adsorbent are much lower for the polymeric adsorbent.

7.7.1.3 Post-Treatment Requirement--

Assuming effluent goals are realized, the post-treatment requirements are restricted to treatment of the regeneration effluent. Other possible waste streams requiring further processing could include the washing effluents (if required for the prerinse and/or postrinse of the resin), the regeneration solvent containing the organics removed from the feed stream, and the condensed regeneration steam containing dissolved organics. Requirements will depend upon the process scheme used.

7.7.1.4 Treatment Combinations--

Resin adsorption will normally be given consideration in applications for which carbon adsorption would be considered as a potentially viable treatment alternative. However, it will not generally be economically competitive with carbon adsorption. In certain situations a combination of resin and carbon adsorption could be used to advantage. For example it may be attractive as a polishing step to remove specific contaminants (particularly if the contaminants have recovery value) passing a carbon adsorption bed, e.g., polar, low molecular weight compounds.

7.7.2 Demonstrated Performance

Resin adsorption technology is not as established as activated carbon adsorption is for full scale treatment of waste streams containing organic solvents and other low molecular weight organic contaminants. Studies have been conducted to determine the performance of resins as adsorbents for several types of organic chemical compounds. The results of one such study (Reference 7) are as follows:

1. Alcohols - Polymeric resins have provided complete removal of several alcohols at 100 μg/L concentrations.
2. Aliphatics - The adsorption of several chemical groups by polymeric resins was, in order of decreasing adsorbability, aldehydes and ketones, alcohols, chlorinated aromatics, aromatics, amines, and chlorinated alkenes and alkanes. Adsorption of aliphatics ranged from 25-100 percent. All but the chlorinated alkanes and chlorinated alkenes were removed more readily by resin than by activated carbon.
3. Amines - Complete adsorption of amines at 100 μg/L concentrations was reported. Resin adsorbents were more effective than activated carbon adsorbents.
4. Aromatics - A polymeric resin, Amberlite XAD-2, was found to adsorb aromatics more effectively than did activated carbon.

These results were the basis for Table 7.7.3 which identifies those solvent and ignitable organic compounds that have been readily addressed by polymeric resins. These results are not all inclusive and should only be used as a basis for further study.

TABLE 7.7.3. CHEMICAL COMPOUNDS TREATED BY RESIN ADSORPTION

	Priority solvents	Other solvents	Ignitables
Aldehydes and Ketones	Acetone Cyclohexanone Methyl ethyl ketone Methyl isobutyl ketone	-----	Chloroacetaldehyde Ethanol Formaldehyde Glycidylaldehyde Paraldehyde
Alcohols	1-Butanol Cresols Isobutyl alcohol Methanol	2-Ethoxy ethanol Propylene glycol	Allyl alcohol Thio methanol
Chlorinated Aromatics	Chlorobenzene 1,2-Dichlorobenzene	o-Dichlorobenzene	-----
Aromatics	Ethylbenzene Nitrobenzene Pyridine Toluene Xylene	Benzene Cyclohexane 1,4-Dioxane 2-Picoline	Cumene
Esters	Ethyl acetate Ethyl ether	Bis(chloromethyl)ether Ethyl carbamate Furan Furfural Tetrahydrofuran	Acrolein Acrylic acid 2-2'-Bioxirane Chloromethyl methyl ether Epichlorohydrin Ethyl acrylate Ethyl methacrylate Methyl chlorocarbonate Methyl isocyanate Methyl methacrylate Oxirane

(continued)

TABLE 7.7.3 (continued)

	Priority solvents	Other solvents	Ignitables
Amines	-----	Acetonitrile Aniline 2-Nitropropane	Dimethylamine Dipropylamine Ethylene diamine Ethylenimine Methacrylonitrile 2-Methyl aziridine n-Propylamine
Chlorinated Alkanes and Alkenes	Methylene chloride Tetrachloroethylene 1,1,1-Trichloroethane 1,1,2-Trichloro-1,2,2-tri-fluoroethane Trichloroethene Trichloromonofluoromethane	Dichlorodifluoromethane 1,1-Dichloroethylene 1,2-Dichloroethylene 1,2-Dichloropropane 1,3-Dichloropropene 1,4-Dichloro-2-butene Ethylene dichloride Ethylidene dichloride Hexachloroethane 1,1,1,2-Tetrachloroethane 1,1,2,2-Tetrachloroethane 1,1,2-Trichloroethane	Chloroprene
Miscellaneous	Carbon disulfide Carbon tetrachloride	Bromoform Chloroform	Allyl chloride Methyl bromide 1-Methylbutadiene Methyl chloride

Source: References 7 through 10.

A U.S. EPA study examined the adsorption capacity of Ambersorb XE-340 and compared these data to that of granular activated carbon adsorption. Table 7.7.4 shows the adsorption capacity of Ambersorb XE-340. The capacities of the resin adsorbent were generally higher than those shown by the carbon adsorbent for these constituents under similar test conditions.

Table 7.7.5 shows the adsorption capacity of Ambersorb XE-340 for several solvents and concentration ranges. The results of a pilot study investigating treatment methods for ground water contaminated by chlorinated solvents, namely 1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene are shown in Table 7.7.6. A direct comparison can be made between Ambersorb XE-340 and two carbons from ICI and Calgon. Figure 7.7.2, graphically illustrates the removal of the organics from the influent in the pilot plant investigation to yield a low concentration effluent.

7.7.3 Cost of Resin Adsorption

Resin adsorbents are quite expensive (Table 7.7.7). The cost exceeds that of granular activated carbon (GAC) ($0.80 to $1.00 per pound). However, the economics of using resins or polymeric adsorbents may in certain cases be more favorable than those for granular activated carbon.

Thermal regeneration costs for GAC adsorption systems are quite high and carbon losses are of the order of 3 to 9 percent per regeneration. Even though macroreticular (resin) adsorbents cost more per pound, they are relatively cheaper to regenerate and regeneration does not result in any appreciable adsorbent loss. Thus, smaller beds and more frequent regenerations may be economically viable with resin adsorbents.

Design criteria for a one million gallon per day treatment plant are shown in Table 7.7.8. Assuming influent concentrations of 300-1,000 ppb, the operation is designed to remove greater than 90 percent of the incoming contaminant. A comparable GAC system is analyzed simultaneously for comparison. The capital and operating costs for each system are given in Table 7.7.9. It can be seen that both the capital investment and the operating costs are lower when the more expensive (by volume) adsorbent is used. This comes about primarily because fewer and smaller contactors are utilized and expensive thermal regeneration furnaces are not required.

TABLE 7.7.4. ADSORPTION OF SOLVENTS BY AMBERSORB XE-340

	Average concentration, µg/L	Bed depth, m (ft)	Empty bed contact time, minutes	Loading to 0.1 µg/L breakthrough, m^3/m^3[a]
Trichloroethylene	215	0.3 (1)	2	83,700[b]
	210	0.6 (2)	4	78,600[b]
	210	1.2 (4)	7.5	53,300[b]
	177	0.8 (2.5)	9	>20,160
	4	0.8 (2.5)	8.5	>123,340
	3	0.2 (0.8)	5	>117,000
Tetrachloroethylene	41	0.3 (1)	2	>99,900[b]
	51	0.6 (2)	4	78,600[b]
	65	1.2 (4)	7.5	>53,300[b]
	70	0.3 (1)	2	106,000[b]
	94	0.8 (2.5)	5	112,900
	1,400	0.8 (2.5)	9	17,920
	3	0.8 (2.5)	8.5	>123,340
	2	0.8 (2.5)	9	>20,160
1,1,1-Trichloroethane	5	1.2 (4)	7.5	39,300[b]
	33	0.8 (2.5)	9	56,000
	237	0.2 (0.8)	5	82,600
	23	0.2 (0.8)	5	100,800
	1	0.8 (2.5)	9	20,160
Carbon Tetrachloride	19	0.8 (2.5)	5	7,560
	19	0.8 (2.5)	10	15,120

(continued)

TABLE 7.7.4 (continued)

	Average concentration, μg/L	Bed depth, m (ft)	Empty bed contact time, minutes	Loading to 0.1 μg/L breakthrough, m^3/m^3[a]
Cis-1,2-Dichloroethylene	40	0.3 (1)	2	37,200[b]
	38	0.6 (2)	4	39,500[b]
	40	1.2 (4)	7.5	19,700[b]
	40	0.3 (1)	2	36,400[b]
	25	0.8 (2.5)	6	14,400
	22	0.8 (2.5)	6	7,200
	16	0.8 (2.5)	6	11,500
	6	0.8 (2.5)	9	20,160
	2	0.8 (2.5)	8.5	59,000 but 123,340
1,1-Dichloroethylene	122	0.2 (0.8)	5	80,600
	4	0.2 (0.8)	5	110,800

[a] m^3 water/m^3 carbon.

[b] Breakthrough defined by shape of wavefront curve; generally 20 to 25 μg/1 of contaminant in adsorbent effluent.

Source: U.S. EPA. Treatment of Volatile Organic Compounds in Drinking Water, EPA-600/8-83-019. May 1983.

TABLE 7.7.5. REMOVAL OF CHLORINATED SOLVENTS BY AMBERSORB XE-340

Compound	Concentration range (μg/L)	Flow rate (gpm/ft^3)	EBCT[b] (min)	BV[c] to 10% leakage	TOC (mg/L)
Carbon Tetrachloride	nf - 87[a]	1.5	5	14,976	---
Chloroform	64 - 95	1.5	5	6,048	---
1,1-Dichloroethylene	41 - 74	1.5	5	>42,000	0.5
1,2-Dichloroethylene	5 - 28	1.2	6.2	4,645	---
1,2-Dichloroethylene	<1 - 4	0.9	8.5	>58,108	---
1,2-Dichloroethylene	3 - 9	0.8	9	20,160	0.5
Tetrachloroethylene	60 - 205	1.5	5	>42,000	0.5
Tetrachloroethylene	597 - 2,500	0.88	8.5	17,788	---
1,1,1-Trichloroethane	172 - 286	1.5	5	>42,000	0.5
1,1,1-Trichloroethane	11 - 214	0.9	8.5	>58,100	---
Trichloroethylene	1 - 2	1.5	5	>42,000	0.5
Trichloroethylene	1 - 10	0.9	8.5	>58,100	---
Trichloroethylene	120 - 276	0.8	9	>20,100	0.5

[a] nf = Not found.

[b] EBCT = Empty Bed Contact Time.

[c] BV = Bed Volume (m^3 water/m^3 carbon).

Source: Reference 10.

TABLE 7.7.6. PILOT PLANT ADSORPTION SUMMARY

Column	Adsorbent	Cycle number	Flow rate	Compound	Bed volumes to 10% leakage (leakage ppb)	Days
1	ICI Carbon	1	2 gpm/ft^3	1,2-Dichloroethylene	15,000 (4)	40
1	ICI Carbon	1	2 gpm/ft^3	Trichloroethylene	25,700 (17)	67
1	ICI Carbon	1	2 gpm/ft^3	Tetrachloroethylene	35,300 (6)	92
----Steam Regeneration----						
1	ICI Carbon	2	2 gpm/ft^3	1,2-Dichloroethylene	5,000 (4)	13
1	ICI Carbon	2	2 gpm/ft^3	Trichloroethylene	14,200 (15)	37
1	ICI Carbon	2	2 gpm/ft^3	Tetrachloroethylene	>35,300 (9)	92
2	Calgon Carbon	1	2 gpm/ft^3	1,2-Dichloroethylene	17,300 (4)	45
2	Calgon Carbon	1	2 gpm/ft^3	Trichloroethylene	38,400 (17)	100
2	Calgon Carbon	1	2 gpm/ft^3	Tetrachloroethylene	>49,000 (6)	130
----Steam Regeneration----						
2	Calgon Carbon	2	2 gpm/ft^3	1,2-Dichloroethylene	3,000	8
2	Calgon Carbon	2	2 gpm/ft^3	Trichloroethylene	17,000 (15)	44
2	Calgon Carbon	2	2 gpm/ft^3	Tetrachloroethylene	>21,000 (12)	55
3	Ambersorb XE-340	1	4 gpm/ft^3	1,2-Dichloroethylene	27,000 (5)	35
3	Ambersorb XE-340	1	4 gpm/ft^3	Trichloroethylene	105,000 (17)	137
3	Ambersorb XE-340	1	4 gpm/ft^3	Tetrachloroethylene	121,000 (7)	158
----Steam Regeneration----						
3	Ambersorb XE-340	2	4 gpm/ft^3	1,2-Dichloroethylene	38,400 (7)	50
3	Ambersorb XE-340	2	4 gpm/ft^3	Trichloroethylene	46,000 (13)	60
3	Ambersorb XE-340	2	4 gpm/ft^3	Tetrachloroethylene	46,000 (17)	60

(continued)

TABLE 7.7.6 (continued)

Column	Adsorbent	Cycle number	Flow rate	Compound	Bed volumes to 10% leakage (leakage ppb)	Days
4	Ambersorb XE-340	1	4 gpm/ft^3	1,2-Dichloroethylene	31,000 (7)	40
4	Ambersorb XE-340	1	4 gpm/ft^3	Trichloroethylene	69,000 (13)	90
4	Ambersorb XE-340	1	4 gpm/ft^3	Tetrachloroethylene	>77,000 (7)	100
5	Ambersorb XE-340	1	2 gpm/ft^3	1,2-Dichloroethylene	40,000 (4)	104
5	Ambersorb XE-340	1	2 gpm/ft^3	Trichloroethylene	80,000 (20)	208
5	Ambersorb XE-340	1	2 gpm/ft^3	Tetrachloroethylene	83,000 (6)	216
----Steam Regeneration----						
5	Ambersorb XE-340	2	2 gpm/ft^3	1,2-Dichloroethylene	23,000 (6)	60
5	Ambersorb XE-340	2	2 gpm/ft^3	Trichloroethylene	23,000 (17)	60
5	Ambersorb XE-340	2	2 gpm/ft^3	Tetrachloroethylene	23,000 (9)	60
----This Column was stopped prematurely and then Steam Regenerated----						
5	Ambersorb XE-340	3	4 gpm/ft^3	1,2-Dichloroethylene	15,000 (4)	20
5	Ambersorb XE-340	3	4 gpm/ft^3	Trichloroethylene	69,000 (17)	90
5	Ambersorb XE-340	3	4 gpm/ft^3	Tetrachloroethylene	77,000 (6)	100
----Steam Regeneration----						
5	Ambersorb XE-340	4	4 gpm/ft^3	1,2-Dichloroethylene	28,000 (5)	36
5	Ambersorb XE-340	4	4 gpm/ft^3	Trichloroethylene	64,000 (16)	83
5	Ambersorb XE-340	4	4 gpm/ft^3	Tetrachloroethylene	73,000 (11)	95

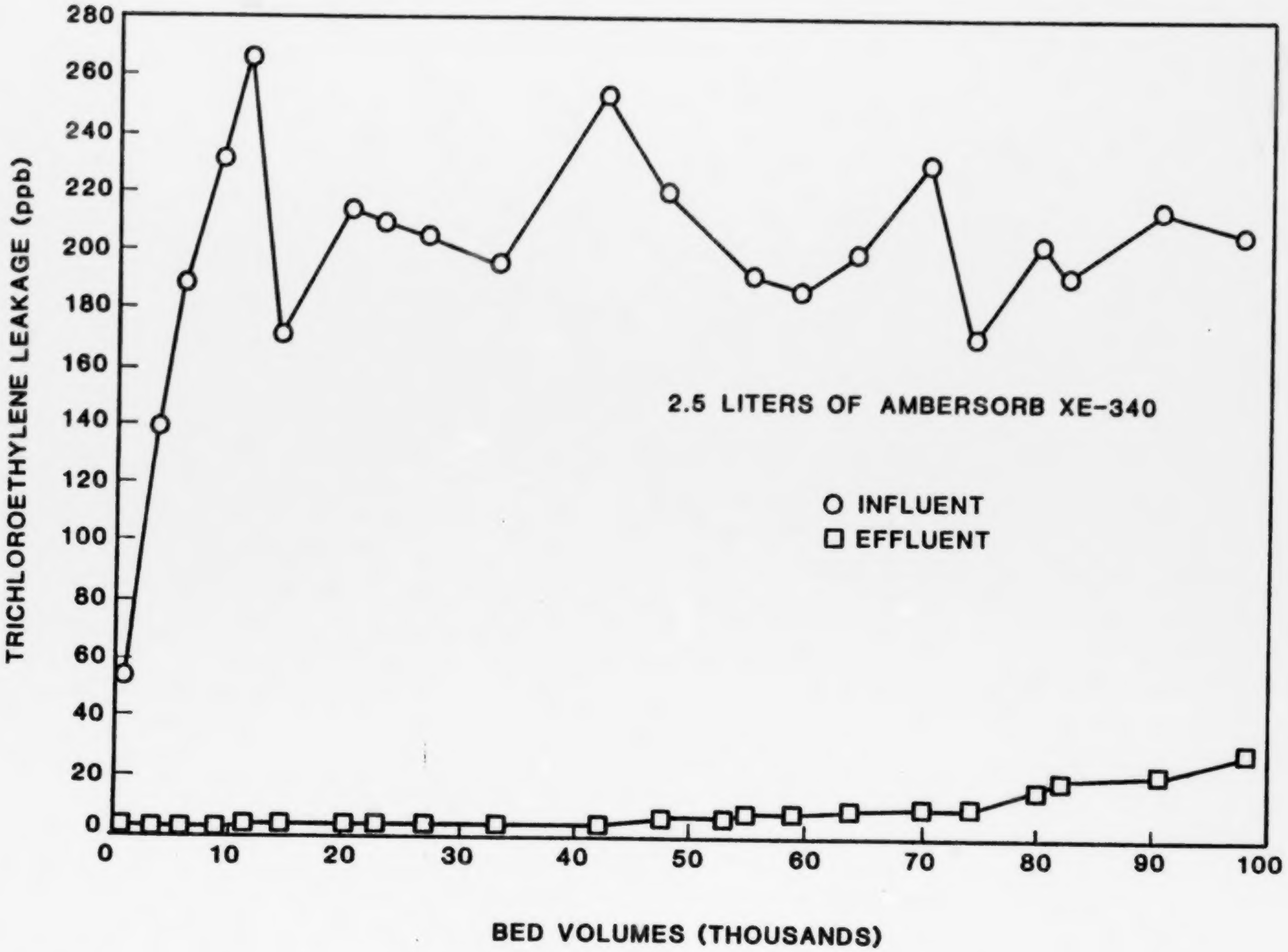


Figure 7.7.2. Performance of resin adsorption bed.

TABLE 7.7.7. COST OF ADSORBENTS[a]

Adsorbent	Chemical nature	Cost $/ft^3[b]
Amberlite XAD-2	Polystyrene	282.95
Amberlite XAD-4	Polystyrene	355.05
Amberlite XAD-7	Acrylic ester	223.25
Amberlite XAD-8	Acrylic ester	337.25

[a] Personal communication with Rohm and Haas Company, Fluid Process Chemicals Department, Philadelphia, PA, April 3, 1986.

[b] At a Bulk Density of 37 lbs/ft^3, costs are roughly $6 to $10 per pound.

TABLE 7.7.8. DESIGN CRITERIA--TRIHALOMETHANE REMOVAL

Parameter	Adsorbent Ambersorb XE-340	 Granular activated carbon
Density	37 lb/ft^3	25 lb/ft^3
Nominal Flowrate	6.0 gpm/ft^3 1.25-min EBCT[a]	1.0 gpm/ft^3 7.48-min EBCT[a]
Contactors	58 ft^3 each 2 on-stream 1 regeneration/standby	348 ft^3 each 2 on-stream 1 regeneration 1 standby
On-stream Time	3.3 days	20 days
Regeneration		
Type	in-place steam	thermal reactivation
Time/Contactor	8 hr	11 days
Absorbent Lifetime	5 yr (fouling limited)	8 months @ 8% loss/cycle

Design Basis: 1.0 mgd average flow, 1.43 mgd peak flow.

[a] Empty bed contact time.

Source: References 11 and 12.

TABLE 7.7.9. COST COMPARISON--GAC VS. RESIN[a]

1.0 mgd Plant

Capital Cost	Resin	Granular Activated Carbon
Contactor, Pumps, Regeneration Facilities Plus 25% for Engineering Contingencies	$350,000	$950,000
Adsorbent Cost		
	$ 45,000 @ $7.00/lb	$ 20,000 @ $0.55/lb
Total	395,000	$970,000

Operating Costs	$/yr	¢/1,000 gal	$/yr	¢/1,000 gal
Adsorber Power	7,100	1.945	3,550	0.973
Regeneration Fuel	3,000	0.822	4,203	1.152
Solvent Regeneration	6,188	1.695	---	---
Adsorbent Makeup	9,000	2.466	18,000	4.932
	(5 yr)		(8% loss/cycle)	
Subtotal	$25,288	6.928	$25,753	7.057
Capital Related Costs (exclude adsorbent):				
Depreciation 9%	49,000	13.420	133,000	36.438
Maintenance 3%				
Property Overhead 2%				
Quality Control	9,000	2.460	9,000	2.460
Total	$83,288	22.8¢/ 1,000 gal	$167,753	46.0¢/ 1,000 gal

[a]No specific GAC or resin product. Values taken at average costs.

Source: References 11 and 12.

The resin system looks very promising because of the many assumptions made concerning design and performance, e.g., high capacity, rapid kinetics, and a 5 year resin lifetime. The assumptions have not yet been demonstrated. Moreover, the design is for a waste influent loading (1 ppm) that is extremely low for an industrial waste stream. Costs, already high relative to many other technologies, will increase drastically as influent loadings (and system size) increase.

However, the example does indicate that resin adsorption may be more economical than carbon adsorption. Similar reasoning has been applied in Reference 1 where costs have been estimated for resin adsorption applied to three different waste streams. Costs ranged from $38.60 per 1,000 gallons for a phenol recovery system (at 5 percent phenol in waste) to $0.83 per 1,000 gallons for a chlorinated pesticide removal system. In the latter case, the cost of a GAC treatment system was estimated at $1.33 per 1,000 gallons. The cost data are outdated (from the 1970s); costs in 1986 dollars would be about 50 percent greater, based on changes in the chemical engineering plant cost index.

The high costs of resin adsorption for the treatment of moderate to high concentration contaminant levels can only be justified in situations where cost benefit is realized from product recovery. In the case of the phenol recovery system used in the example above, credit from the sale of phenol exceeded total annual operating costs, therefore justifying use of the process on an economics basis.

7.7.4 Overall Status

7.7.4.1 Availability--

Resin adsorption technology parallels that for carbon adsorption. Equipment requirements are similar and available from a number of manufacturers serving the chemical process industries. However, there appears to be some question about the commercial availability of many of the resin adsorbents for which data are reported in the literature. Ambersorb XE-340, for example, manufactured by Rohm and Haas and the subject of numerous technical studies, is not available in commercial quantities. The availability of some other resin adsorbents may also be questionable.

7.7.4.2 Application--

Because of their expense, resins are not commonly used full-scale to remove organics from wastewaters.[6] There is also little publicly available information on current or proposed industrial applications. Information of a general nature does report that resins are being used for color removal from dyestuff and paper mill waste streams, for phenol removal, and for polishing of high purity waters.

The following applicants have been identified as being particularly attractive for resin adsorption technology.[1]

- Treatment of highly colored wastes where color is associated with organic compounds
- Material recovery where solvents of commercial value are present in high enough concentration to warrant material recovery since it is relatively easy to recover solutes from resin adsorbents
- Where selective adsorption is an advantage and resins can be tailored to meet selectivity needs
- Where low leakage rates are required; resins exhibit low leakage apparently as a result of rapid adsorption kinetics
- Where carbon regenerations is not practical, e.g., in cases when thermal regeneration is not safe
- Where the waste stream contains high levels of inorganic dissolved solids which drastically lowers carbon activity; resins activity can usually be retained ,although prerinses may be required

7.7.4.3 Environmental Impacts--

The only major environmental impacts resulting from resin adsorption systems are associated with the disposal of the regeneration solution and the extracted solutes when they can not be recycled. Distillation to recover solvent and incineration of the separated solute are likely treatment/disposal options. Air emissions would have to be considered as a result of these treatment processes.

7.7.4.4 Advantages and Limitations--

As noted, resin adsorption appears to offer advantages in certain situations; e.g., for treatment of highly colored wastes, for material recovery, where low leakage is required, and in instances where carbon adsorption is not practical. The advantages of resin adsorption are a result of their potential for selectively, rapid adsorption kinetics, and ease of chemical regeneration.

Major limitations of resin adsorbents result from: 1) the generally lower surface area and usually lower adsorption capacities than those found in activated carbon; 2) their susceptibility to fouling due to poisoning by materials that are not removed by the regenerant; and 3) their relatively high cost. The high cost of the resin may be balanced by its ease of regeneration and their predicted long lifetimes in situations where carbon must be thermally regenerated and carbon losses become appreciable (up to 10 percent).

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SECTION 8.0

CHEMICAL TREATMENT PROCESSES

The chemical treatment methods discussed in this section include some processes which could equally well be classified as thermal processes (i.e., wet air and supercritical water oxidation) since the general result of these high temperature processes is the conversion of the organic contaminants to fundamental products of oxidation such as carbon dioxide and water. Other technologies like the experimental UV/ozonation process and other oxidation processes do not achieve total destruction and must be considered as a pretreatment step for a second treatment technology, usually a biotreatment process. Chlorinolysis, another process discussed in this section, is unique in that it utilizes chlorinated organic wastes to produce a product, namely carbon tetrachloride. The processes addressed in this section are:

8.1 Wet Air Oxidation

8.2 Supercritical Water Oxidation

8.3 Ozonation

8.4 Other Chemical Oxidation Processes

8.5 Chlorinolysis

8.6 Dechlorination Processes

Discussions of these chemical treatment processes are provided using the same format as was used for the discussions of physical treatment processes in the previous section.

8.1 WET AIR OXIDATION

Wet air oxidation (WAO) is the oxidation of dissolved or suspended contaminants in aqueous waste streams at elevated temperatures and pressures. It is generally considered applicable for the treatment of certain organic-containing media that are too toxic to treat biologically and yet too dilute to incinerate economically.[1,2] A leading manufacturer of commercially available WAO equipment reports that WAO takes place at temperatures of 175 to 320°C (347 to 608°F) and pressures of 2,169 to 20,708 kPa (300 to 3000 psig).[1] Although the process is operated at subcritical conditions (i.e., below 374°C and 218 atmospheres), the high temperatures and the high solubility of oxygen in the aqueous phase greatly enhances the reaction rates over those experienced at lower temperatures and pressures. In practice, the three variables of pressure, temperature and time are controlled to achieve the desired reductions in contaminant levels.

In addition to serving as the source of oxygen for the process, the aqueous phase also moderates the reaction rates by providing a medium for heat transfer and heat dissipation through vaporization. Generally, pressures are maintained above the vapor pressure of water to limit water evaporation rates, thus limiting the heat requirement for the process. The reactions proceed without the need for auxiliary fuel at feed chemical oxygen demand (COD) concentrations of 20 to 30 grams per liter.[3] The extent of contaminant destruction will depend upon the wastes to be oxidized and the reaction conditions. Typically, 80 percent of the organic contaminants will be oxidized to CO_2 and H_2O. Residual organics will generally be low molecular weight, biodegradable compounds such as acetic acid and formic acid.

8.1.1 Process Description

A schematic of a continuous WAO system is shown in Figure 8.1.1.[4] The Zimmerman WAO System,[5] as shown in the figure, has been developed by Zimpro, Inc., Rothschild, Wisconsin. It represents an established technology for the treatment of municipal sludges and certain industrial wastes. Full scale treatment of solvent wastes has not yet been demonstrated. However a 10 gpm

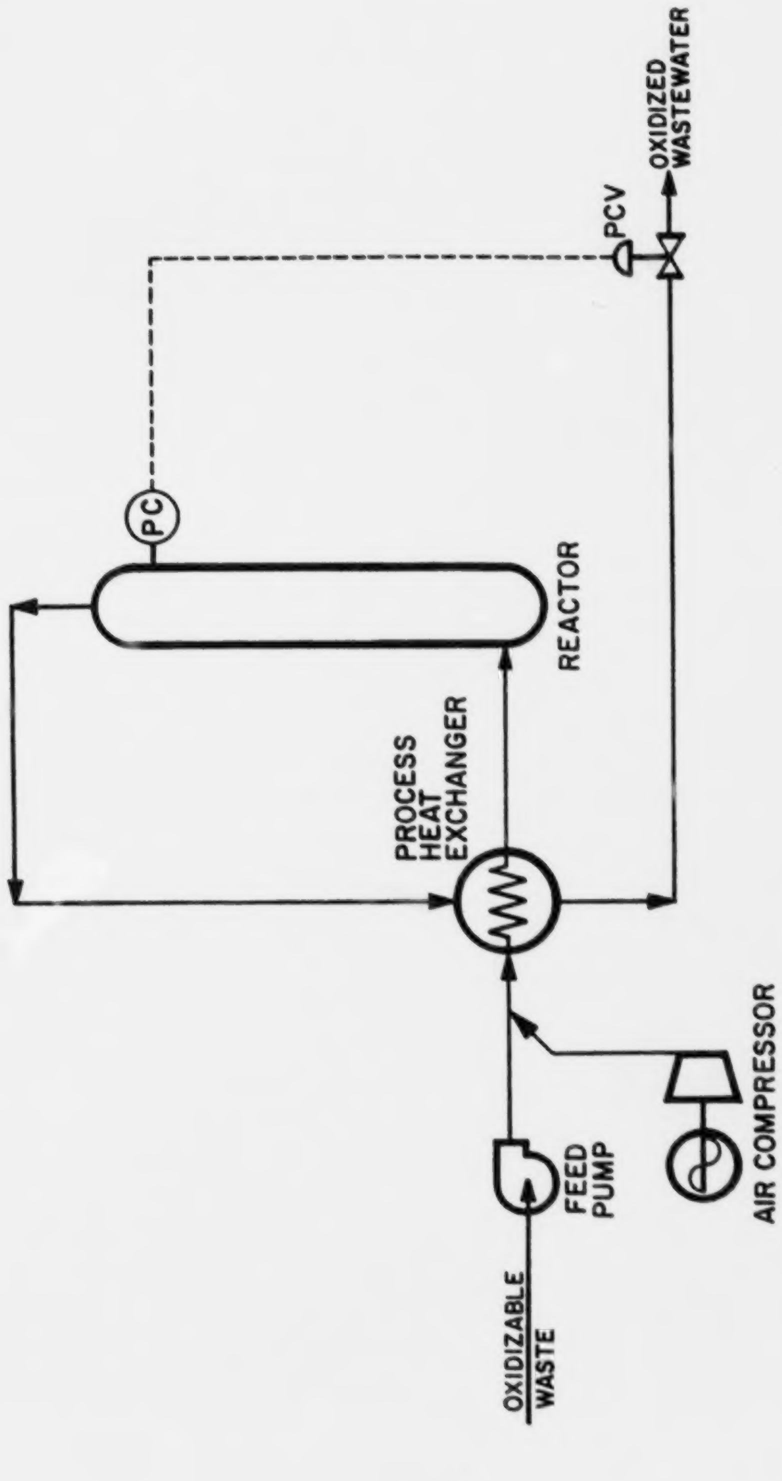

Figure 8.1.1. Wet air oxidation general flow diagram
Source: Reference 4

pilot unit has been used to treat an alkaline solvent waste and a solvent still bottom waste, as well as other organic wastes, at a commercial waste treatment facility in California.[3,6-8] As will be noted later, the effectiveness of WAO as an alternative to land disposal for certain solvent containing waste streams will depend upon a number of factors including the molecular structure and concentration of the contaminants and the processing conditions.[1,3,6-12]

In the WAO process, the waste stream containing oxidizable contaminants is pumped to the reactor using a positive displacement, high pressure pump. The feed stream is preheated by heat exchange with the hot, treated effluent stream. Air (or pure oxygen) is injected following the high pressure pump, and as shown in the figure, usually directly into the reactor vessel. Steam is added as required to increase the temperature within the reactor to a level necessary to support the oxidation reactions in the unit. As oxidation proceeds, heat of combustion is liberated. At feed COD concentrations of roughly 2 percent the heat of combustion will generally be sufficient to bring about a temperature rise and some vaporization of volatile components. Depending upon the temperature of the effluent following heat exchange with the feed stream, energy recovery may be possible or final cooling may be required. Following energy removal, the oxidized effluent, consisting mainly of water, carbon dioxide, and nitrogen, is reduced in pressure through a specially designed automatic control valve. The effluent liquor is either suitable for final discharge (contaminant reduction achieves treatment standards) or is now readily biodegradable and can be piped to a biotreatment unit for further reduction of contamination levels. Similarly, noncondensible gases can either be released to the atmosphere or passed through a secondary control device (e.g., carbon adsorption unit) if additional treatment is required to reduce air contaminant emissions to acceptable levels.[8]

The pressure vessel is sized to accommodate a fixed waste flow and residence time. Based on the characteristics of the waste, a combination of time, temperature, pressure, and possibly catalyst can be utilized to bring about the destruction of many solvent contaminants.

The continuous reactor can reportedly take two forms: a tower reactor[1] or a reactor consisting of a cascade of completely stirred tank reactors (CSTRs).[13] The bubble tower reactor is by far the more common. It is a vertical reactor, as shown in Figure 8.1.1, in which air is passed through the feed. The reactor is sized, based on feed rate, to provide the holding time required for the reactions to proceed to design levels. The stirred tank cascade reactor consists of a series of horizontal reactor chambers contained within a horizontal cylinder. The wastewater cascades from one chamber to the next, and then is released for discharge or post-treatment. Air is generally injected into each of the CSTRs.

8.1.1.1 Pretreatment Requirements for Different Waste Forms and Characteristics--

Very little discussion is found in the literature concerning the physical form of wastes treatable by WAO. However, WAO equipment and designs have been used successfully to treat a number of municipal and industrial sludges. According to a representative of the leading manufacturer of WAO systems, wastes containing up to 15 percent COD (roughly equivalent to 7 to 8 percent organics) are now being treated successfully in commercial equipment.[14]

Treatment of solid bearing wastes is dependent upon selection of suitable pump designs and control devices. WAO units used for activated carbon regeneration now operate at the 5 to 6 percent solids range.[14] Treatment of higher solid levels is not precluded by fundamental process or design limitations. Column design must also be consistent with the need to avoid settling within the column under operating flow conditions. Thus, pretreatment to remove high density solids (e.g., metals by precipitation) and accomplish size reduction (e.g. filtration, gravity setting) would be required for some slurries. It should be noted that the WAO unit operated by Casmalia Resources in California does not accept slurries or sludges for treatment. This may be a result of design factors precluding their introduction into the system.[15]

Several bench scale studies have been conducted to determine the susceptibility of specific compounds to wet air oxidations. Results of these studies and other studies have been summarized in the literature.[1,8,10,16]

The results indicate that the following types of compounds can be destroyed in wet air oxidation units.

- Aliphatic compounds, including those with multiple halogen atoms. Depending upon the severity of treatment, some residual oxygenated compounds such as low molecular weight alcohols, aldehydes, ketones, and carboxylic acids might be present, but these are readily biotreatable.
- Aromatic hydrocarbons, such as toluene and pyrene are easily oxidized.
- Halogenated aromatics can be oxidized provided there is at least one nonhalogen functional group present on the ring; the group should be an electron donating constituent such as an hydroxyl, amino, or methyl group.
- Halogenated aromatics, such as 1,2-dichlorobenzene, PCBs, and TCDDs, are resistant to oxidation under conventional conditions although these compounds are destroyed to a greater extent as conditions are made more severe or catalysts are employed. However, Casmalia Resources does not accept chlorinated aromatics.[13]
- Casmalia Resources also does not accept for WAO treatment wastes containing highly volatile organics like Freon which would enter the unit in the gas phase, and tin, which is corrosive to heat exchanger surfaces.[13]

Batch process results obtained in the laboratory are applicable to continuous process design for pure compounds and complex sludges, i.e., specific compound destruction is similar and predictable for pure compounds and those compounds contained in complex industrial wastes.[1,17]

8.1.1.2 Operating Parameters--

Although operation of a WAO system is possible, by definition, under all subcritical conditions; i.e., below 374°C and 218 atm (3220 psig), commercially available equipment is designed to operate at temperatures ranging from 175 to 320°C and at pressures of 300 to 3000 psig.[1]

Of all variables affecting WAO, temperature has the greatest effect on reaction rates. In most cases, about 150°C (300°F) is the lower limit for appreciable reaction. About 250°C (482°F) is needed for 80 percent reduction of COD, and at least 300°C (572°F) is needed for 95 percent reduction of COD within practical reaction times. Destruction rates for specific constituents may be greater or less than that shown for COD reductions.[2]

Initial reaction rates and rates druing the first 30 minutes are relatively fast. After about 60 minutes, rates become so slow that generally little increase in percent oxidation is gained in extended reaction.[2]

An increase in reaction temperature will lead to increased oxidation but generally will require an increase in system pressure to maintain the liquid phase and promote wet oxidation. A drawback to increasing the temperature and pressure of the reaction is the greater stress placed on the equipment and its components, e.g., the increased potential for corrosion problems. Corrosion is controlled by the use of corrosion resistant materials such as titanium.

As noted by Zimmerman, et al., the object of WAO is to intimately mix the right portion of air with the feed, so that under the required pressure, combustion will occur at a speed and temperature which will effectively reduce the organic waste to desired levels. Pressures should be maintained at a level that will provide an oxygen rich liquid phase so that oxidation is maintained.[5] Charts and curves are provided in this reference[5] to aid in the determination of waste heating value, stoichiometric oxygen requirement, and the distribution of water between the liquid and vapor phases at given temperatures and pressures.

Previous experience with the design of wet oxidation systems has shown that batch results are applicable to continuous process design when the oxygen transfer efficiency is 90 percent (11 percent excess air) or less. A model was developed to gain insight into the key system parameters using a common industrial waste stream and fixed temperature, residence time, and COD reduction. The model was used to estimate costs for the system.[17] Its value, as a predictive tool, along with that of supplementary kinetic studies[18] of batch wet oxidation, is limited by the sparsity of experimental data concerning reaction products and their phase distributions at the elevated temperatures and pressures encountered during WAO.

8.1.1.3 Post-Treatment Requirements--

The use of WAO to meet EPA treatment levels (see Table 2.2) for solvent wastes has not yet been demonstrated.[8] As will be noted later, WAO has been used under certain conditions to achieve destruction levels that meet the EPA proposed treatment standards. However, for the most part, this level of performance has been achieved for specific compounds oxidized in batch reactors under conditions that are more rigorous than those normally used in commercial systems.

Destruction levels will vary for different compounds in complex waste mixtures and there is evidence that certain of the low molecular weight WAO breakdown products (e.g., methanol, acetone, acetaldehyde, formic acid, etc.) are resistant to further oxidation. Thus, under typical WAO operating conditions it is likely that both contaminant residuals and low molecular weight process by-product residuals may be present. While it is entirely possible that imposition of more stringent operating conditions will serve to reduce these residuals to acceptable levels, the manufacturers and users of commercial WAO systems stress that the major applications involve the pretreatment of waste, usually for subsequent biological treatment.

Even under conditions that are favorable for wet oxidation, it is also likely that certain contaminants, particularly some of the more volatile components, will partition between the vapor phase and the liquid phase. The partitioning will be a function of operating conditions and the contaminant partial pressure. The Henry's Law constant at the temperature of operation will fix the distribution, however, Henry's Law constant is not generally known under most conditions of WAO system operation. Although a method of estimation has been proposed by researchers at Michigan Technological University,[18] empirical tests will be necessary to establish vapor and liquid phase residuals and some post-treatment of both streams may be necessary. Existing post-treatment methods for the liquid generally involves bacteriological treatment. Although the results of post-treatment schemes for vapors from the WAO system have not been found in the literature, a two-stage water scrubber/activated carbon adsorption system has been used to treat WAO vapor emissions.[3] Presumably carbon adsorption or scrubbing systems could be routinely employed if necessary.

8.1.1.4 Treatment System Combinations--

Most of the commercial WAO systems in operation today are employed as pretreatment devices to enhance the biotreatability of municipal and industrial wastes. Wet air oxidation is also used as a means of regenerating spent activated carbon used as an adsorbent. In the latter case the WAO regenerates the activated carbon through oxidation of the organics adsorbed on the carbon surfaces.[19]

The application of WAO to industrial organic wastes has generally been limited to treating specific, homogeneous waste streams, including soda pulping liquors at pulp mills and n-nitrosodimethylamine and acrylonitrile wastes. However, WAO has been used since 1983 to treat varied waste streams at the Casmalia Class I disposal site, located near Santa Maria, California. Phenolic, solvent still bottoms, and other organic wastes have all been treated at Casmalia, in certain instances in conjunction with a powdered activated carbon treatment system and a two stage scrubber-carbon adsorption system for vapor treatment.[20]

Treatment of specific waste streams to meet EPA solvent treatment standards by a WAO system is not precluded, as evidenced by some of the performance data shown below for removal of specific contaminants. However, in most instances reaction conditions would have to be tailored to the waste stream and pollutant. Generally an increase in the pressure/temperature conditions normally employed by the users of WAO systems would be required. Equipment problems associated with the more stringent operating conditions would have to be considered.

8.1.2 Demonstrated Performance of WAO Systems

As noted by EPA,[8] full scale use of WAO technology is well demonstrated for the treatment of municipal sludge but full scale treatment of solvent wastes is not demonstrated. However, data showing the WAO destruction of specific organic compounds including several solvents of concern to EPA, have been provided in the literature. These data are largely the result of bench scale testing, but do include results of pilot-scale and full-scale performance tests. The data indicate that WAO can be effective in treating specific organic contaminants, including many solvents and various industrial wastewaters. However, not all specific contaminants are destroyed to the extent that direct discharge would be allowable under the proposed EPA treatment standards for solvents of concern. Chlorinated organics appear to be the most difficult compounds to destroy. Residuals in both the gas and liquid phase would also have to be considered on a case by case basis if WAO technology is to be used for the treatment of specific solvent containing waste streams.

8.1.2.1 Bench-Scale Studies--

Bench scale studies of the destruction of specific organic substances by wet oxidation have been conducted at Zimpro, Inc.[1,8,16] Some of these data are shown in Tables 8.1.1 through 8.1.3. The tables include destruction data for organic compounds other than the solvents and ignitable organics of interest to this study in order to illustrate the effect of operating variables, catalysts, and chemical structure on the effectiveness of wet air oxidation.

The data shown in Table 8.1.1 were taken from Reference 16. The results were obtained using single pure compounds in distilled water as the material undergoing treatment. Concentrations of starting material at 5 to 12 g/L were used for the study. Batch oxidations were carried out in a titanium 3.8 liter (1-gallon) magna-drive stirred autoclave. Temperature regulation was achieved with a controller-recorder that regulated the external heating elements. Generally, one liter of material was charged into the autoclave, which was sealed and pressurized with compressed air. After heating to the desired temperature for one hour, the contents were cooled by an internal coil carrying cold water. The resulting gases were analyzed to determine oxygen use and the contents were removed for further testing. The test and analytical procedures used are identified in the reference, although no data are provided with regard to the excess air used and the pressures realized during the 1 hour test period.

As shown in Table 8.1.1, all 10 compounds (only two of which, acrolein and acrylonitrile are considered as solvents/ignitables) were destroyed to an appreciable extent at 320°C and at 275°C, although a soluble copper catalyst was required for extensive destruction of 2-chlorophenol and pentachlorophenol at 275°C. These two chlorinated aromatics were the most difficult to destroy

TABLE 8.1.1. ONE HOUR WET OXIDATIONS

Compound	Starting Concentration (g/L)	Percent starting material destroyed		
		320°C	275°C	275°C/Cu++
Acenapthene	7.0	99.96	99.9	--
Acrolein	8.41	99.96[a]	99.05	--
Acrylonitrile	8.06	99.91	99.00	99.50
2-chlorophenol	12.41	99.86	94.96	99.88
2,4-dimethylphenol	8.22	99.99	99.99	--
2-4-dinitrotoluene	10.0	99.8	99.74	--
1,2-diphenylhydrazine	5.0	99.98	99.98	--
4-nitrophenol	10.0	99.96	99.60	--
Pentachlorophenol	5.0	99.88	81.96	97.30
Phenol	10.0	99.97	99.77	--

[a] The concentration remaining was less than the detection limit of 3 mg/L.

TABLE 8.1.2. PRODUCTS IDENTIFIED FROM ONE HOUR OXIDATIONS AT 320°C

Starting compounds	Formic acid (mg/L)	Acetic acid (mg/L)
Acenapthene	6	443
Acrolein	81	862
Acrylonitrile	48	921
2-chlorophenol	52	442
2,4-dimethylphenol	75	1,527
2-4-dinitrotoluene	134	213
1,2-diphenylhydrazine	37	526
4-nitrophenol	793	500
Pentachlorophenol	0	101
Phenol	13	1,034

TABLE 8.1.3. BENCH-SCALE WET AIR OXIDATION OF PURE COMPOUNDS

Compound	Wet oxidation conditions °C/minutes	Starting concentration (mg/L)	Final concentraion (mg/L)	Percent destroyed
Arochlor 1254	320/120	20,000	7,400	63.0
Carbon Tetrachloride	275/60	4,330	12	99.7
Chlorobenzene	[a]275/60	5,535	1,550	72.0
Chloroform	275/60	4,450	3	99.9
1-Chloronaphthalene	[a]275/60	5,970	5	99.92
Dibutylphthalate	275/60	5,320	26	99.5
2,4-Dichloroaniline	[a]275/60	259	0.5	99.8
1,2-Dichlorobenzene	[a]320/60	6,530	2,017	69.1
1,2-Dichloroethane	275/60	6,280	13	99.8
Formic Acid	300/60	25,000	410	98.3
Hexachlorocyclopentadiene	300/60	10,000	15	99.9
Isophorone	275/60	4,650	29	99.4
Kepone	[a]280/60	1,000	690	31.0
Malathion	250/60	11,800	18	99.85
Toluene	275/60	4,330	12	99.7
Nitrobenzene	[a]320/120	5,125	255	95.0
N-Nitrosodimethylamine	275/60	5,030	22	99.5
Pyrene	275/60	500	0.26	99.95
Pyridine	[a]320/120	3,910	570	85.4
2,4,6-Trichloroaniline	[a]320/120	10,000	2.5	99.97

[a] Catalyzed.

and unlike the other compounds continued to show a marked increase in destruction efficiency with temperature through the 275°C to 320°C range. Presumably destruction efficiencies would be somewhat higher at more elevated temperatures.

Although no attempt was made to measure vapor phase residuals, Reference 16 does present data for liquid phase residuals. While the details of analysis are not specified and it is not entirely certain that other residual compounds are not formed, only formic acid and acetic acid were identified in the amounts shown in Table 8.1.2. Although these residuals represent as much as 20 weight percent of the original charge of the specific test compound, the two low molecular weight acids formed are readily biodegradable by conventional treatment methods. Thus, it was concluded that wet oxidation of the waste constituents followed by biotreatment would yield an effluent suitable for discharge to a publicly owned treatment plant.

Additional specific organic compound data taken from References 1 and 8 are shown in Table 8.1.3. As stated in Reference 1, bench-scale studies were performed using batch autoclaves having a total volume of 500 to 750 mL, and constructed of 316L stainless steel, nickel, or titanium. The autoclaves were charged with 100 to 300 mL of the sample to be oxidized, sealed, charged with air or oxygen sufficient to satisfy the sample oxygen demand, and then subjected to a controlled time/temperature cycle. Continuous agitation was provided during the treatment period.

As shown in Table 8.1.3 the chlorinated aromatic compounds (e.g., kepone, Arochlor 1254, 1,2-dichlorobenzene, and chlorobenzene) were resistant to degradation, whereas the lower molecular weight chlorinated aliphatics (e.g., chloroform, carbon tetrachloride, and 1,2-dichloroethane), including several solvents of concern, were relatively easy to destroy. Reference 8 presents data showing destruction efficiencies in excess of 99 percent for Arochlor 1254 and other chlorinated aromatics using a proprietary catalyst system. No data were presented for liquid or vapor phase residuals.

Bench-scale wet oxidation studies were also performed on industrial wastewaters in which the destruction of specific organic contaminants was monitored. The results, as shown in Table 8.1.4, indicate that all compounds, with the exception of the one halogenated aromatic organic tested, 1,2-dichlorobenzene, undergo significant oxidation. However, the residual

TABLE 8.1.4. BENCH-SCALE WET AIR OXIDATION OF ORGANICS IN WASTEWATERS

Compound	Wet air oxidation conditions °C/min	Feed concentration (mg/L)	Product concentration (mg/L)	Removal (%)
Dimethylaniline	280/60	1,300	1.6	99.9
Toluene	320/120	5.0	0.5	90.+
Acetonitrile	[a]275/60	1,040	17	98.4
Propionitrile	[a]275/60	391	7	98.2
2,4-Dichlorophenol	320/60	500	2	99.6
Dipropylformamide	250/60	219	1	99.5
N-nitrosodimethylamine	320/60	510	1	99.8
Trichloroethylene	320/60	500	1.7	99.7
1,2-Dichlorobenzene	320/120	540	150	72.2

[a] Catalyzed.

concentration of one solvent of concern, trichloroethylene, is higher than the proposed EPA treatment standard (0.1 mg/liter) and thus would require additional treatment before discharge. The residual concentration of 150 mg/liter found for 1,2-dichlorobenzene is well above the proposed EPA treatment standard of 2 mg/liter. This is consistent with the pure compound WAO results presented in Table 8.1.3.

Results of the WAO of several solvents in wastewaters have also been reported in Reference 1, and are shown in Table 8.1.5. The compounds measured were either present in the wastewater, or in the case of the chlorinated compound tested in study 3, added as spikes to industrial wastewater. Again, the data show the difficulty in oxidizing the halogenated aromatic compound, chlorobenzene. The low molecular weight alcohols also exhibit resistance to WAO.

Results of wet oxidation tests involving the use of a patented catalyst consisting of bromide, nitrate, and manganese ions in acidic solution have also been reported in the literature.[21] Batch tests were conducted using a 1-liter titanium autoclave. Compounds studied include solvents of concern such as nitrobenzene and xylene as well as other low molecular weight compounds such as ethylene dibromide, acetonitrile, hexachlorobutadiene, and trichloropropane. Reaction temperatures used were somewhat lower than those used in the Zimpro studies. Destruction efficiencies were also low, e.g., 54 percent of xylene destroyed at 165°C and up to 31 percent of nitrobenzene destroyed after 1 hour at 200°C. Some reaction product data were also presented and discussed. It was noted that HCl is a byproduct of the wet air oxidation of chlorinated compounds and thus some provisions must be made for removal of this compound from the reaction products.

8.1.2.2 Pilot-Scale Studies--

The results of several pilot scale studies have been reported in the literature.[11] The flow rates of systems used in these studies ranged from 2.5 to 28.9 gallons per hour (0.23 to 2.6 cubic meters per day). In a pilot

TABLE 8.1.5. BENCH-SCALE WET AIR OXIDATION OF WASTEWATERS

Study	Compound	Concentration (mg/L) Feed	Oxidized 280°C/60 min	Oxidized 320°C/60 min	Percent removal at 280°C
1	Acetone	1,680	10	10	99.4
1	Ethanol	1,530	60	10	96.1
1	Methyl Ethyl Ketone	276	1	3	99.6
1	Methanol	3,230	1,380	290	57.3
1	2-Propanol	2,230	40	30	98.2
1	Toluene	80	1	1	98.8
2	Ethanol	2,800	1,200	--	57.1
2	Methyl Ethyl Ketone	8,200	1	--	99.9
2	2-Propanol	9,900	170	--	98.2
3	Chloroform	270	1	--	99.6
3	Chlorobenzene	792	61	--	92.3
3	Trichloroethylene	300	2	--	99.3
3	Dichloromethane	252	1	--	99.6

scale test of coke plant wastewater, removals of phenols and cresol were measured at 99.8 and 99.9+ percent, respectively. The test was carried out at 279°C, 1558 psig, and a flow rate of 6.3 gallons per hour. Residence time was 69 minutes and a catalyst was used to assist the reaction.[1]

Pilot-scale tests were also conducted with a wastewater containing many specific organic solvents of concern along with pesticide and herbicide wastes. The results of this pilot-scale WAO are presented in Table 8.1.6. Destruction efficiencies were generally high, even for 1,2-dichlorobenzene, a compound that was not readily oxidized in the bench-scale tests.

8.1.2.3 Full-Scale Studies--

Several full-scale studies have been conducted at the Casmalia Resources facility in Santa Barbara County, California using a skid mounted WAO systems, capable of 10 gallon per minute flow rate for waste materials with a COD of 40 g/liter. Tests have been conducted on wastewater containing phenolics, organic sulfur, cyanides, nonhalogenated pesticides, solvent still bottoms, and general organics. In the case of the general organic wastewater, COD was reduced 96.7 percent to a level of 2.5 g/liter.[4] During this test the wet oxidation unit was operated at 277°C (531°F), 1550 psig, and a residence time of 120 minutes.[2] For the solvent still bottoms, the unit was operated at an average reactor temperature of 268°C (514°F), a reactor pressure of 1550 psig, and a nominal residence time of 118 minutes. COD, BOD, and TOC reductions of 95.3, 93.8, and 96.1 percent, respectively, were measured.[2] Although no specific organic compound destruction efficiencies were reported for solvents of concern, phenol destruction efficiencies of 99.8 percent were reported in a test of a spent caustic waste from a petroleum refinery.[1]

8.1.2.4 Studies of Treatment Systems Using WAO--

The use of pilot-scale and full-scale treatment systems combining PACT^{TM} (powdered activated carbon addition to the reaction basin of an activated sludge process) with wet air oxidation regeneration have been reported in the literature.[19,22] Reference 22 reports destruction efficiencies of greater than 99 percent for several priority pollutant solvents present in a domestic and organic chemical wastewater not treatable by conventional biological treatment systems.

TABLE 8.1.6. PILOT-SCALE WET AIR OXIDATION OF ORGANIC COMPOUNDS IN INDUSTRIAL WASTEWATER

Wet Air Oxidation Conditions:	
Temperature, °C	314
Flow, gph	2.6
Residence Time, min	128
Pressure, psig	1,943
COD	
Feed, g/liter	77.5
Effluent, g/liter	9.4
% Removal	87.9
1,2-dichlorobenzene	
Feed, mg/liter	2,213
Effluent, mg/liter	29
% Removal	98.7
Methylene Chloride	
Feed, mg/liter	60
Effluent, mg/liter	0.01
% Removal	99.9+
Perchloroethylene	
Feed, mg/liter	4,000
Effluent, mg/liter	0.9
% Removal	99.9+
Freon TF	
Feed, mg/liter	3,000
Effluent, mg/liter	2
% Removal	99.9+
Xylene	
Feed, mg/liter	8,385
Effluent, mg/liter	20
% Removal	99.8+
Toluene	
Feed, mg/liter	30
Effluent, mg/liter	0.5
% Removal	98.3+

(continued)

TABLE 8.1.6 (continued)

Wet Air Oxidation Conditions:	
Temperature, °C	314
Flow, gph	2.6
Residence Time, min	128
Pressure, psig	1,943
Phenols	
Feed, mg/liter	1,556
Effluent, mg/liter	2.1
% Removal	99.9
Isopropyl Alcohol	
Feed, mg/liter	1,700
Effluent, mg/liter	400
% Removal	76.5
Methyl Ethyl Ketone	
Feed, mg/liter	6,000
Effluent, mg/liter	1.0
% Removal	99.9+

S.I. Conversion
m^3/d = gph x 0.0908
kPa = psig x 6.89

Source: Reference 1.

As noted in Reference 22, the PACT^{TM}/Wet Air Regeneration pilot system was operated at aeration detention times of 2.5 to 5.5 hours and at wet air regeneration temperatures of 230 C.

Initial testing of conventional biological treatment systems and sludge digestion confirmed the inability of a pure biological system to treat the test wastewater. The BOD_5 to COD ratio, an indicator of biotreatability, averaged 0.35 (a ratio of 0.5 to 0.6 for domestic wastes is common) and over 72 EPA priority pollutants were detected in the raw wastewater. An activated sludge pilot plant operating at a 9 hour hydraulic retention time provided marginal organic removal (56% COD reduction) and was unable to produce an effluent with less than the required 25 mg/L suspended solids. Variations in waste strength prevented accurate system control and dictated a need for waste equalization. Attempts to anaerobically digest the waste activated sludge were not successful due to the presence of toxic components. The PACT^{TM} effluent was analyzed for priority pollutants. The results (Table 8.1.7) show high priority pollutant removal through the PACT^{TM}/Wet Air Regeneration treatment system.[22] Many of the treatment levels achieved are below the EPA treatment standards for specific solvents.

Reference 19 presents results obtained during treatment of RCRA wastewater and CERCLA ground water at the Bofors-Nobel facility in Muskegon, Michigan. Cleanup at the site was conducted in accordance with the system schematic shown in Figure 8.1.2. Two WAO units are used, one dedicated solely to detoxification, the other used primarily as a carbon regeneration unit with occasional use as an additional detoxification unit. Although no data are provided for specific organic solvent components of the waste, an average efficiency of 99.8 percent is stated for toxics in the feed.

8.1.3 Cost of Treatment

8.1.3.1 Wet Air Oxidation Costs--

Treatment costs for wet air oxidation systems will be affected by a number of parameters including the amount of oxidation occurring, the hydraulic flow, the design operating conditions necessary to meet the treatment objectives, and the materials of construction. These factors account for the band of capital costs shown in Figure 8.1.3. The figure was

TABLE 8.1.7. PRIORITY POLLUTANT REMOVALS USING A PACT^{TM}/WET AIR REGENERATION SYSTEM FOR DOMESTIC AND ORGANIC CHEMICALS WASTEWATER[a]

Parameter	Influent (μg/L)	Effluent (μg/L)	Removal efficiency (%)
Benzene	907	3.0	99.6
Chlorobenzene	597	3.7	99.3
1,2,4-Trichlorobenzene	62	ND	100
1,1,1-Trichloroethane	7	ND	100
Chloroform[b]	87	25	71
2-Chlorophenol	98	ND	100
1,2-Dichlorobenzene	113	ND	100
1,3-Dichlorobenzene	67	ND	100
Ethylbenzene	26	ND	97
Methylchloride[c]	11	91	--
Dichlorobromomethane	2.3	ND	100
Nitrobenzene	ND	ND	--
Tetrachloroethylene	1	ND	100
Toluene	1,195	2	99.8

[a] 4.0 hour aeration time.

[b] Drinking water background exceeds 50Mμg/L chloroform.

[c] Effluent numbers suspect due to possible laboratory background interference.

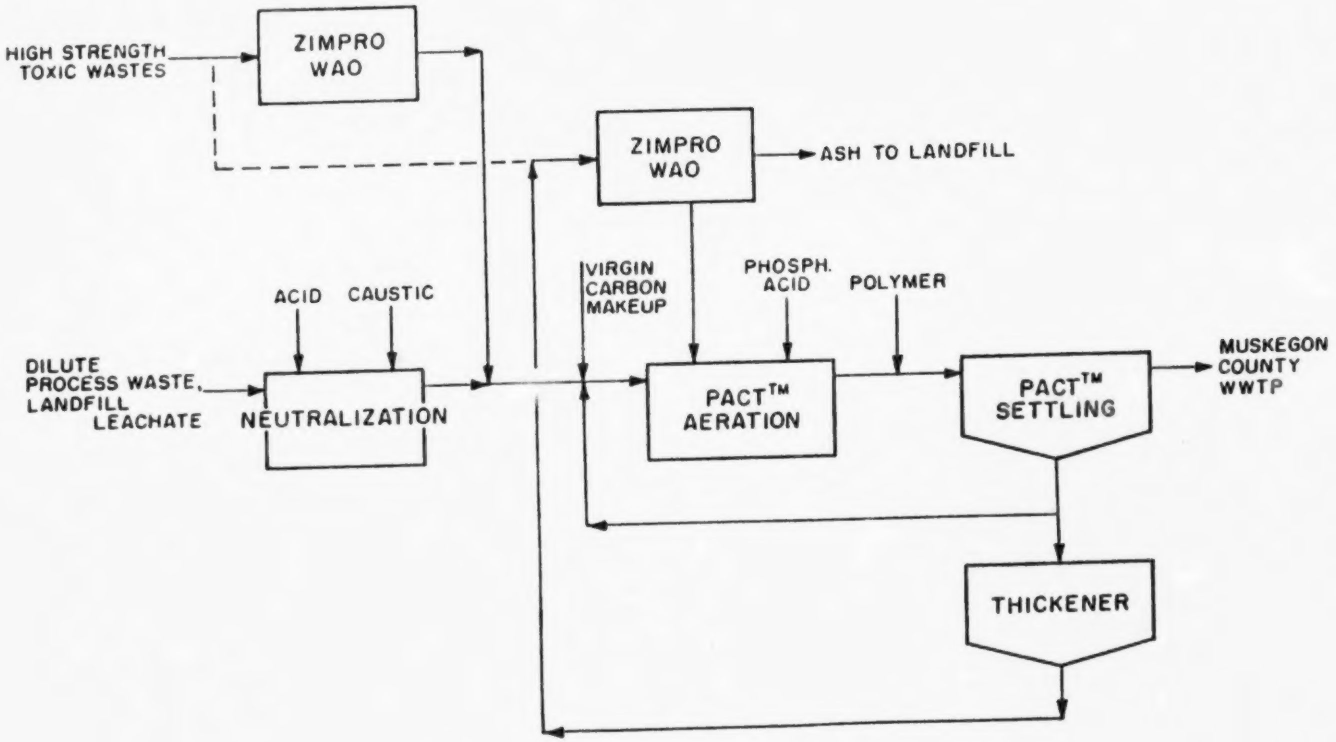

Figure 8.1.2. 4.5 MGD wastewater treatment facility
Source: Reference 19

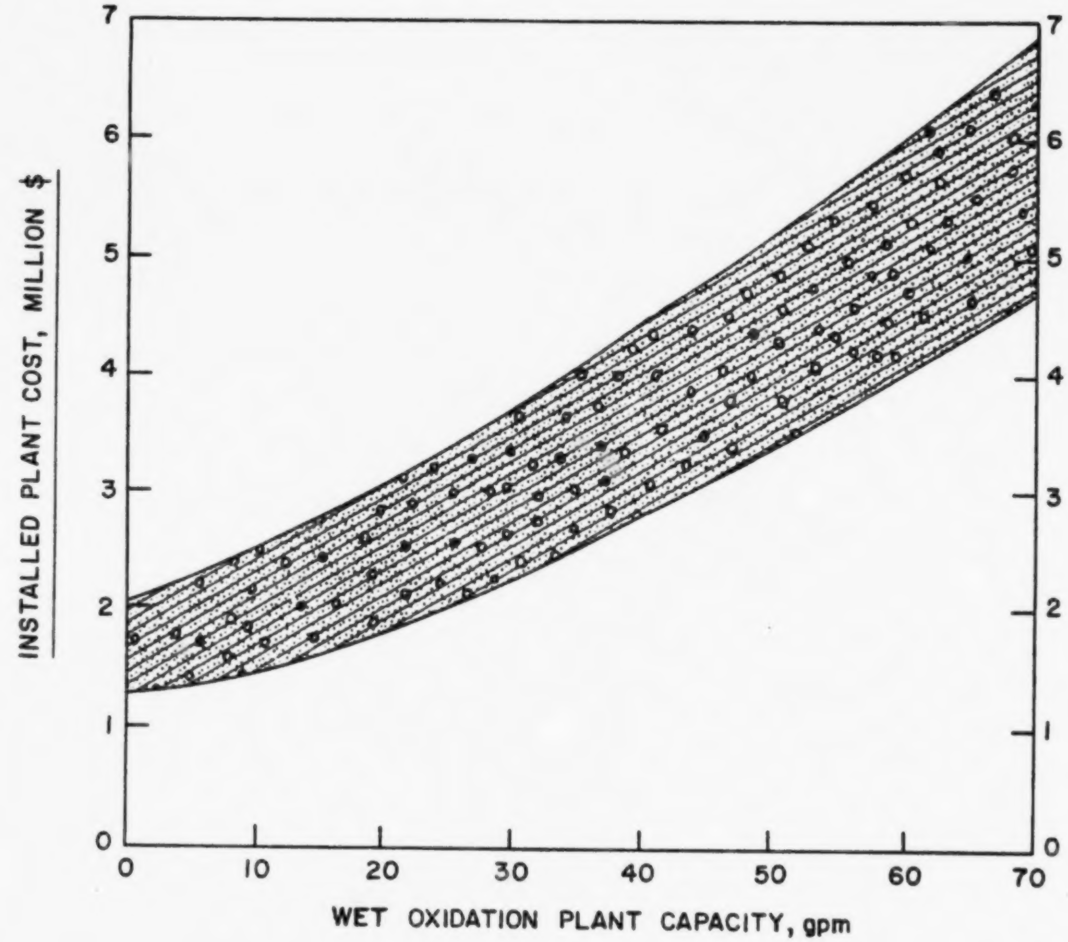

Figure 8.1.3. Installed plant costs versus capacity.

taken from Reference 2 and updated to reflect changes in the 1982 to 1986 Chemical Engineering (CE) plant cost index. The costs do not include any costs associated with pretreatment of the feed or post-treatment of the vapor phase component of the treated liquor. However, post-treatment costs were included in another capital cost estimate of $2.45 million (adjusted to 1986 using the CE plant cost index) for a 20 gpm plant.[4] This estimate is within the capital cost band shown in Figure 8.1.3.

Operating costs for the wet oxidation unit are shown in Figure 8.1.4. These data were also derived from data given in Reference 2 with adjustment made for the costs of labor and cooling water. As noted in Reference 2, power accounts for the largest element of cost. This power cost is primarily the result of air compressor operation. Additional power for supplying energy for the oxidation of very dilute wastewaters would be at most 500 Btu/gallon. The associated costs for this energy would be less than one (1) cent/gallon.

Total costs, capital plus operating, on a per unit of feed basis, requires assumptions on life cycle, depreciation, taxes, and current interest rates for the capital cost. One avenue for financing that has been used commercially, common lease terms, are 5 years and 20 percent value at end of term.* Table 8.1.8 illustrates the effect on total costs per unit of feed.

TABLE 8.1.8. WAO COSTS VERSUS FLOW

Hydraulic flow (gpm)	Cost elements per gallon, cents		
	operating	capital	total
2.0	23	31	54
10	6	7	13
20	3	5	8
40	2-3	4-5	6-8

At Casmalia Resources, the prices, (April, 1985) for treatment of wastes are computed based on the oxygen demand of the material. Prices range from a minimum of $120 per ton to a maximum of $700 per ton versus $15 per ton for the land disposal of low risk wastes.[15]

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*Assume lease charges of $17/1000 per month based on total installed cost.

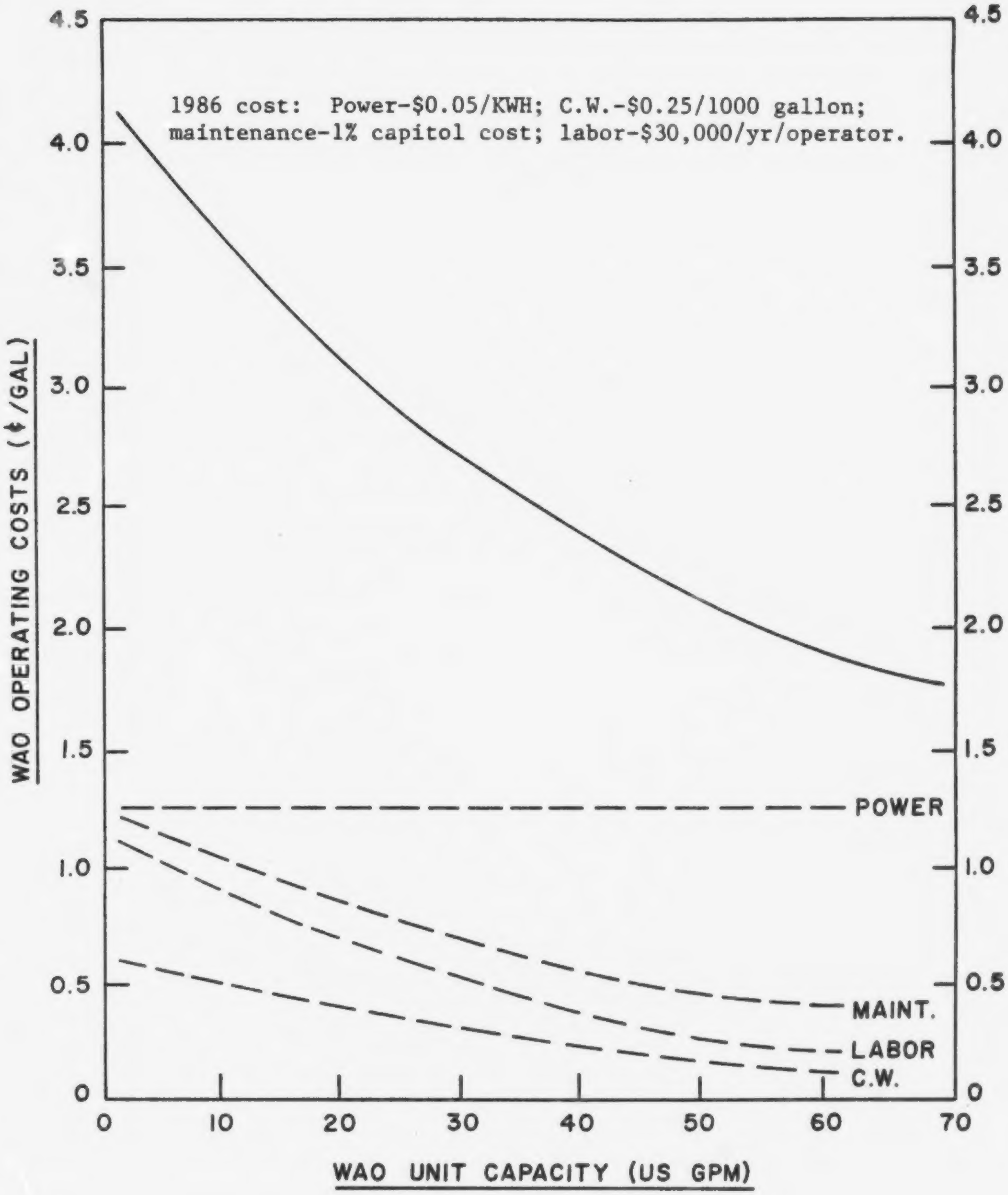

Figure 8.1.4. Unit operating costs versus unit flow rate.

8.1.3.2 Comparison of WAO Costs with Other Alternative Treatment Costs--

A cost comparison between a 20 gpm WAO system and a comparable incinerator was presented in Reference 4 for a wastewater containing 7 percent COD. It was concluded that, although the installed capital cost for WAO was 50 percent higher than that for incineration, operating costs were appreciably less ($132,000 annual operating cost for WAO versus $463,500 for incineration in 1979 dollars) despite a charge for scrubbing of the WAO off gases and an operating surcharge for BOD discharges to an average municipal wastewater treatment plant. It was concluded that total operating costs including amortization favor WAO when the fuel value of the waste organics is low (less than approximately 50 g/liter Chemical Oxygen Demand).[4]

Other sources of cost data, including comparative costs, are References 3 and 17. Reference 3 states that WAO is generally less expensive than incineration when the COD concentration ranges between 10 to 150 g/liter. Rough cost estimates of from about 10 to 50 cents per gallon were proposed depending upon type of waste, concentration, and amount to be treated. For comparison, landfilling costs of 12 to 25 cents per gallon for drummed wastes were provided. Reference 17 provides cost data for a WAO system designed to treat a 7 percent COD waste at a 10 gallon per minute treatment rate. Net operating costs of $90,780 per year (December 1980) were estimated, a value roughly equivalent to 3 cents per gallon, assuming a zero rate of return on investment. This relatively low operating cost was compared to a landfilling cost of roughly $1 per gallon for barrelled waste and $0.55 to $0.75 per gallon for bulk waste. Although WAO costs were roughly two orders of magnitude greater than typical costs for secondary biological municipal wastewater treatment, the cost of $0.07 per pound of COD removed was suggested as comparable to the typical municipal charge to industry of $0.05 to $0.10 per pound of COD removed.

Another source of cost data, Reference 21, provides data showing that costs are a strong function of the contaminant type, its concentration, and the amount of waste to be treated. Costs ranged from $0.12 per pound of pentachlorophenol to $1.04 per pound of hexachlorobutadiene treated.

8.1.4 Overall Status of WAO Process

8.1.4.1 Availability and Application of WAO Systems--

The WAO process is available commercially, and reportedly well over 150 units are now operating in the field treating municipal and various industrial sludges.[14] The process is used predominately as a pretreatment step to enhance biodegradability. Only a few units are now being used to treat industrial solvent/ignitable wastes. These include the 10 gallon per minute unit at Casmalia Resources in California and other units operating at Bofors-Nobel in Muskegon, Michigan and Northern Petrochemical in Morris, Illinois.

The oxidation of specific contaminants in waste streams by the wet oxidation process is not highly predictable. Equipment manufacturers rely largely on the result of bench-scale results to tailor the design of full-scale WAO continuous units for specific wastes. Full-scale data confirm the results of WAO performance data obtained in bench and pilot-scale studies.[1]

8.1.4.2 Energy and Environmental Impacts--

As noted, the process is thermally self-sustaining when the amount of oxygen uptake is in the 15-20 g/liter range. Below this range, some energy input will be required to initiate and sustain reaction. However, the energy requirement will be appreciably less than that required for incineration.

The environmental impacts of WAO will hinge upon the residuals remaining after treatment. Wet scrubbing and carbon adsorption cleanup systems have been used to treat the HCl formed as a product of chlorinated organic oxidation and to remove volatile organics from the waste off gases. Residuals in the liquid phase may also require post treatment if, for example, 100 percent conversion to CO_2 and H_2O is not realized when treating hydrocarbon contaminants. The available data do suggest that some form of post treatment of both liquid and vapor phases will be required to meet acceptable discharge levels.

8.1.4.3 Advantages and Limitations--

There are several advantages associated with the use of WAO as noted by the developer and stated in Reference 2.

1. The process is thermally self-sustaining when the amount of oxygen uptake is in the 15-20 grams/liter range.
2. The process is well suited for wastes that are too dilute to incinerate economically, yet too toxic to treat biologically.
3. Condensed phase processing requires less equipment volume than gas phase processing.
4. The products of WAO stay in the liquid phase. Offgases from a WAO system are free of NO_x, SO_2, and particulate. Water scrubbing and, if need be, carbon adsorption or fume incineration are used to reduce hydrocarbon emissions or odors.
5. WAO also has application for inorganic compounds combined with organics. The oxidation cleans up the mixture for further removal of the inorganics. WAO can detoxify most of the EPA priority pollutants. Toxic removal parameters are in the order of 99+ percent using short-term, acute, static toxicity measurements.

Limitations of the WAO process relate to the sensitivity of destruction efficiency associated with the chemical nature of the contaminant, the possible influence of metals and other contaminants on performance, the unfavorable economics associated with low and high concentration levels, and the presence of residuals in both the vapor and liquid phases which may require additional treatment. Costly materials of construction and design features may also be required for certain wastes including many of the solvent wastes which will form corrosive reaction products or require extreme temperature/pressure conditions to achieve destruction to acceptable treatment standard levels. In particular, chlorinated aromatic compounds are more resistant to degradation and can result in the production of HCl byproduct.

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8.2 SUPERCRITICAL FLUID OXIDATION

Supercritical fluid oxidation is a technology that has been proposed for the destruction of organic contaminants in wastewaters. It is basically an oxidation process conducted in a water medium at temperatures and pressures that are supercritical for water; i.e., above 374°C (705°F) and 218 atmospheres. In the supercritical region, water exhibits properties that are far different from liquid water under normal conditions; oxygen and organic compounds become totally miscible with the supercritical water (SCW) and inorganic compounds, such as salts, become very sparingly soluble. When these materials are combined in the SCW process, organics are oxidized and any inorganic salts present in the feed or formed during the oxidation are precipitated from the SCW.

The oxidation reactions proceed rapidly and completely. Reaction times are less than 1 minute, as compared to reaction times of about 60 minutes used in the subcritical wet air oxidation (WAO) process. Moreover, the reaction is essentially complete. Carbon and hydrogen atoms within the organic contaminants are reacted to form CO_2 and H_2O (residuals such as the low molecular weight organic acids and alcohols found in the treated WAO effluent are not found in the SCW process effluent). Heteroatoms (e.g., chlorine and sulfur) are oxidized to their corresponding acidic anion groupings. These anions, and those occurring naturally in the feed, can be neutralized by cation addition to the feed, and the total inorganic content of the waste, save that soluble in the SCW, can be precipitated and recovered by mechanical separators operating at SCW conditions.

8.2.1 Process Description

In the supercritical region, water exhibits properties that are far different from liquid water at normal ambient conditions. The density, dielectric constant, hydrogen bonding, and certain other physical properties change significantly with the result that SCW behaves very much like a moderately polar organic liquid.[1] Thus, solvents such as n-heptane and benzene, for example, become miscible with SCW in all proportions. On the other hand, the solubility of salts such as sodium chloride (NaCl) is as low as 100 ppm and that of calcium chloride ($CaCl_2$) as low as 10 ppm. This is the reverse of the solubilities in water that are found under ambient conditions where the solubilities of NaCl and $CaCl_2$ are about 37 weight percent and up to 70 percent, respectively (Josephson, 1982).

The solubility characteristics of SCW are strongly dependent upon density.[2] A temperature-density diagram is shown in Figure 8.2.1. The critical point which is located on the dome of the vapor-liquid saturation curve is at 374°C and 0.3 gram/cubic centimeter. The supercritical region is that above 374° and the 218 atmosphere isobar. Near the critical point (e.g., between 300° and 450°) the density varies greatly with relatively small changes in temperature at constant pressure.

Insight into the structure of the fluid in this region has been obtained from measurements of the static dielectric constant, values of which are shown in Figure 8.2.1.[3,4] The dielectric constants of some common solvents are given for comparison in Table 8.2.1.

TABLE 8.2.1. DIELECTRIC CONSTANTS OF SOME COMMON SOLVENTS

Carbon dioxide	1.60
n-Hexane	1.89
Benzene	2.28
Ethyl ether	4.34
Ethyl acetate	6.02
Benzyl alcohol	13.1
Ammonia	16.9
Isopropanol	18.3
Acetone	20.7
Ethanol	24.3
Methanol	32.6
Ethylene glycol	37.
Formic acid	58.

Source: Reference 5.

The dielectric constant is a measure of the degree of molecular association. While dielectric constant is not the sole determinant of solubility, the solvent power of water for organics is consistent with variations in the dielectric constant. According to Figure 8.2.1, as

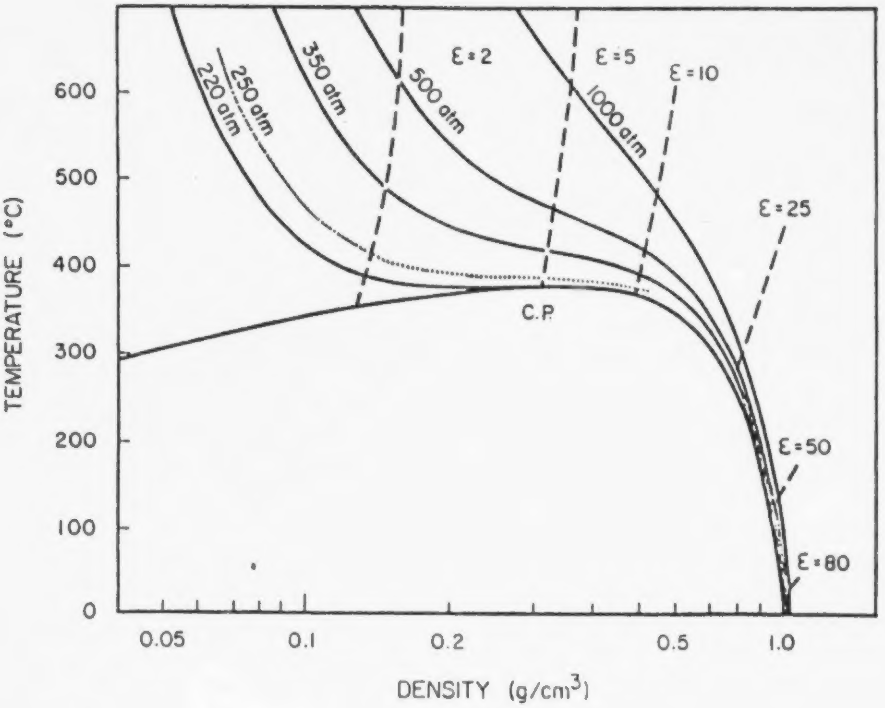

Figure 8.2.1. Temperature-Density Diagram
Source: Reference 2

temperature rises along the saturated liquid-vapor curve the dielectric constant (normally at about 80 due largely to strong hydrogen bonding) decreases rapidly despite only small changes in density. The large decreases in the dielectric reflect the strong dependence of hydrogen bonding forces on distance, with small decreases in density leading to large decreases in dielectric constant. At 130°C ($d= 0.9 g/cm^3$), the dielectric constant is about 50, which is near that of formic acid; at 260°C ($d=0.8 g/cm^3$) the dielectric constant is 25 similar to that of ethanol. At the critical point the dielectric constant is 5, and little, if any, residual hydrogen bonding is present. The major contribution to the dielectric constant is due to dipole-dipole interactions, which gradually decrease with density.[5]

Depending upon the pressure and temperature, the dielectric constant can be varied to achieve values similar to those of moderately polar to nonpolar organic solvents. Solubility behavior parallels the changes in dielectric and at some points supercritical conditions are reached and the components are miscible in all proportions.

The solubilities of inorganic salts in water exhibit different behavior from that shown by the organic compounds. At 250 atmospheres, the solubilities of salts reach a maximum at 350-400°C. Beyond the maximum, the solubilities drop very rapidly with increasing temperature. For example, NaCl solubility is above 40 weight percent at 300°C and 100 ppm at 450°C; $CaCl_2$ has a maximum solubility of 70 percent at subcritical temperatures which drop to 10 ppm at 500°C.[2]

The properties of water, as a function of temperature, are summarized in Figure 8.2.2. The figure shows that water goes through a complete reversal in solubility behavior between 300-500°C. Above 450°C, inorganic salts are practically insoluble, and organic substances are completely miscible.[2]

Given the complete miscibility of oxygen and organic contaminants in the supercritical fluid and the high temperature of operation, oxidation reactions proceed rapidly and completely. In the MODAR process described below, organics, air and water wastes are brought together at 250 atmospheres and at temperatures above 400^oC. The heat of oxidation is released within the fluid and results generally in a rise in temperature to 600-650°C.

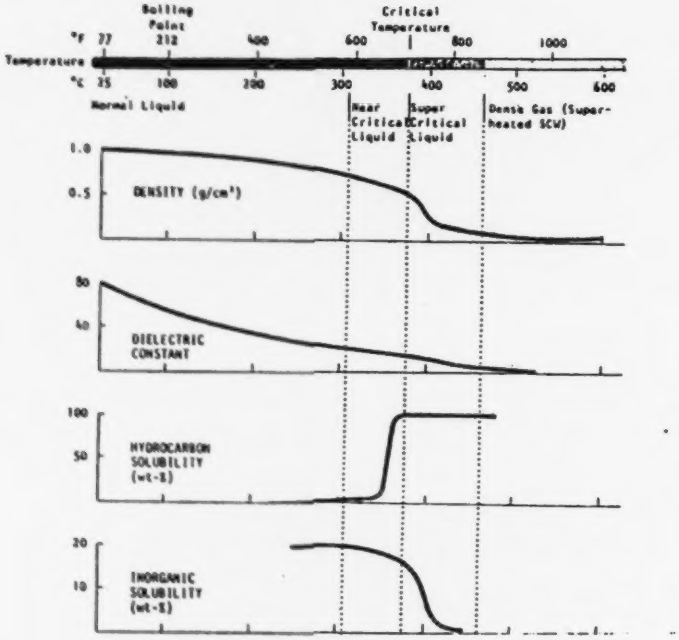

Figure 8.2.2. Properties of water at 250 atm
Source Reference 2

The products of supercritical water reforming are subjected to oxidation while under these homogenous (i.e., single phase) supercritical conditions. The residence time required for oxidation is very short, which greatly reduces the volume of the oxidizer vessel.

When toxic or hazardous organic chemicals are subjected to SCW oxidation, carbon is converted to CO_2 and hydrogen to H_2O. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitrogen compounds will produce nitrogen gas, sulfur is converted to sulfates, phosphorus to phosphates, etc. Upon addition of appropriate cations (e.g., Na+, Mg++, Ca++), inorganic salts are formed.

The heat of oxidation is sufficient to bring the supercritical stream to temperatures in excess of 550°C. At these conditions, inorganic salts have extremely low solubilities in water. Inorganic salts are precipitated out and readily separated from the supercritical fluid phase. After removal of inorganics, the resulting fluid is a highly purified stream of water at high temperature and high pressure. The fluid is used as a source of high-temperature process heat by generating steam.

A schematic flow sheet for the MODAR process as applied to liquid wastes is presented in Figure 8.2.3. This figure and subsequent discussion was provided by MODAR, Inc., (Reference 6).

The process consists of the following steps:

A. Feed

1. Organic waste materials in an aqueous medium are pumped from atmospheric pressure to the pressure in the reaction vessel.

2. Oxygen, stored as a liquid, is pumped to the pressure of the reaction vessel and then vaporized.

3. Feed to the process is controlled to an upper limit heating value of 1800 BTU/lb by adding dilution water or blending higher heating value waste material with lower heating value waste material prior to feeding to the reactor.

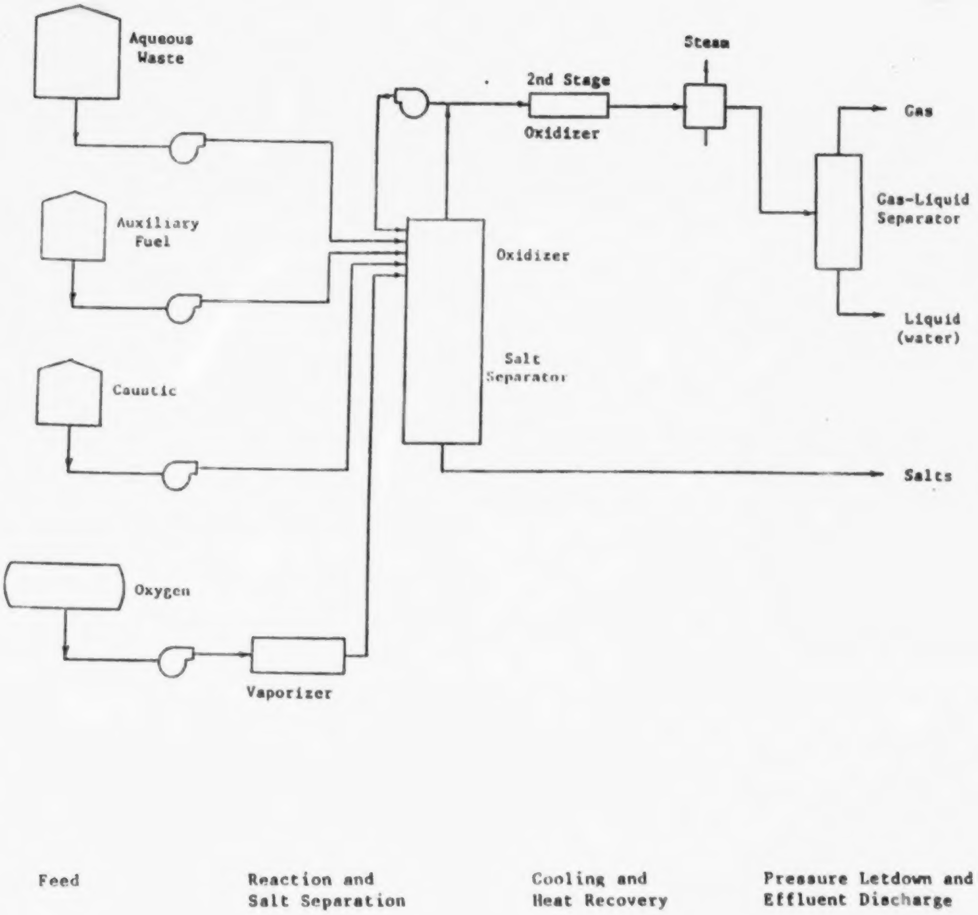

Figure 8.2.3. Schematic flow sheet of MODAR process.
Source: Reference

4. When the aqueous waste has a heating value below 1800 BTU/lb, fuel may be added in order to utilize a cold feed to the oxidizer.

5. Optionally for wastes with heating value below 1800 BTU/lb, a combination of preheat by exchange with process effluent and fuel additon, or preheat alone may be used.

6. When organic wastes contain heteroatoms which produce mineral acids, and it is desired to neutralize these acids and form appropriate salts, caustic is injected as part of the feed stream.

7. A recycle stream of a portion of the supercritical process effluent is mixed with the feed streams to raise the combined fluids to a high enough temperature to ensure that the oxidation reaction goes rapidly to completion.

B. Reaction and Salt Separation

1. Because the water is supercritical, the oxidant is completely miscible with the solution; i.e., the mixture is a single, homogenous phase. Organics are oxidized in a controlled but rapid reaction. Since the oxidizer operates adiabatically, the heat released by the readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly.

2. Since the salts have very low solubility in SCW they separate from the other homogenous fluids and fall to the bottom of the separation vessel where they are removed.

3. The gaseous products of reaction along with the supercritical water leave the reactor at the top. A portion of the supercritical fluid is recycled to the SCW oxidizer by a high temperature, high pressure pump. This operation provides for sufficient heating of the feed to bring the oxidizer influent to optimum reactor conditions.

4. The remaining reactor effluent (other than that recycled) consisting of superheated SCW and carbon dioxide is cooled in order to discharge CO_2 and water at atmospheric conditions.

C. Cooling and Heat Recovery

1. Most of the heat contained in the effluent is used to generate steam for use outside the MODAR Process.

2. The heat remaining in the effluent stream is used for lower level heating requirements and is also dissipated.

D. Pressure Letdown

1. The cooled effluent from the process separates into a liquid water phase and a gaseous phase containing primarily carbon dioxide along with oxygen which is in excess of the stoichiometric requirements.

2. The separation is carried out in multiple stages in order to minimize erosion of valves as well as to optimize equilibria.

3. Salts are removed from the separator as a cool brine through multiple letdown stages and are either dried (and water recovered) or discharged as a brine depending upon client requirements.

8.2.1.1 Pretreatment Requirements--

Very little information exists in the literature to assess pretreatment requirements for the process and its feed streams. The process reportedly can handle slurries, thus, filtration or some other solids removal process may not be required or even desirable if the contaminant is partitioned in the feed between the aqueous phase and the suspended solids. Similarly, the need to remove inorganic constituents may not exist since these constituents will precipitate under the supercritical conditions of operation and presumably will be removed by the mechanical separator shown in Figure 8.2.3. Adverse effects such as interference with pump operations, abrasion of internal parts, and fouling of internal surfaces resulting from existing or formed solids are possible problem areas but were not considered such by MODAR[6].

8.2.1.2 Operating Parameters--

The operating conditions are specified by MODAR as follows:

- Form of Feed Materials: Aqueous slurry or solution of organics.
- Temperature Range: 400°-650°C (750°-1200°F)
- Pressure Range: 220-250 atm
- Residence Time Range: Less than one minute
- Energy Type and Requirements: Thermal, to reaction conditions, with provisions for useful recovery of latent heat of oxidation.

These conditions are capable of achieving destruction efficiencies in excess of 99.999 percent. The technology should be applicable to all solvent/ignitables considered in this TRD. The principal question related to the applicability of the technology is associated with cost, including the durability of the system under the harsh supercritical conditions.

8.2.1.3 Post Treatment Requirements--

Because the oxidation reactions go essentially to completion and provision can be made for neutralization and removal of inorganic products and feed stock components the post treatment requirements should be minimal. Off gases from the subcritical treated effluent should be largely CO_2 and H_2O and liquid effluent residuals will consist mainly of dissolved salts at the 10 to 100 ppm levels.

Along with N_2, N_2O may also be a possible off gas component from the SCW oxidation of nitrogen containing organics. A possible N_2O component would not be considered an air contaminant since there is no evidence involving it in the series of complex chemical reactions producing photochemical smog.[7]

Apart from the modest impacts anticipated as a result of N_2O emissions and the dissolved inorganic salt loading of the liquid effluent the only other residual stream requiring possible attention is the largely solid inorganic stream from the separator. EP toxicity could be a characteristic of possible concern for some wastes.

8.2.1.4 Treatment Combinations-

SCW oxidation systems can be considered for aqueous waste streams containing one or more weight percent of organic constituents. Below 1 percent, other treatment technologies such as adsorption appear to have a cost advantage. The highest practical organic content again will depend upon costs; specifically the cost of SCW oxidation versus incineration for wastes in the 10 to 20 weight percent and higher range. Largely unproven, the SCW oxidation system will, if cost effective, function as a finishing technology discharging effluents that can be expected to meet acceptable levels of discharge.

8.2.2 Demonstrated Performance

The destruction of organic contaminants is a function of reactor temperature and residence time. MODAR reports that a reactor temperature in the range of 600 to 650°C (1120° to 1200°F) and a 5 second residence time are sufficient to achieve destruction efficiencies of 99.999 percent. Higher temperatures could be used to reduce the residence time. However, at a 5 second reaction time, the reactor cost is a small fraction of total capital cost and, thus, there is not much incentive to reduce reactor volume by operating above 650°C.[2]

Theoretically, increasing residence time will also result in increased destruction efficiency. The oxidation kinetics appear to be first order in organic concentration. Assuming perfect mixing and first order kinetics at all concentrations, doubling the residence time could result in a doubling of the destruction efficiency. Thus, a 99.999 percent efficiency could become 99.99999999 (ten nines).

MODAR has conducted more than 200 laboratory (bench) and pilot plant tests in order to study the technical feasibility of SCW oxidation for a variety of organic contaminants. In most cases MODAR does not attempt to measure destruction and removal efficiency to the greatest possible precision. Test objectives are rather to measure the levels of organic carbon in the liquid effluent, and in most cases, residual levels are below detection limits of the analytical equipment. Consequently, destruction removal efficiency, which may be claimed in many of MODAR's tests, are limited to between 99.9% and 99.99+% by precision of the analytical equipment (See Reference 8). When the objective is to demonstrate the maximum degree of waste destruction, richer feeds and more sensitive analytical equipment are used. Tests of this sort (e.g., on dioxins) show destruction and removal efficiencies of more than 99.9999%[6]. Equal or greater destruction efficiencies could be expected for the solvent and other low molecular weight organic compounds of concern.

8.2.3 Cost of Treatment

The most significant operating cost factor is the cost of oxygen consumed. Although compressed air can be used as the source of oxygen, the cost of power as well as the high capital cost of appropriate compressors has led MODAR to use liquefied oxygen as the primary oxygen source. Oxygen demand and heat content of an organic waste are usually directly related, and therefore the heating value of the waste and waste throughput can be used to make a preliminary estimate of waste treatment costs.

Table 8.2.2 presents waste treatment costs based on an aqueous waste with a 10 percent by weight benzene-equivalent and a heat content of 1,800 Btu/lb. This is the optimal heat content of a cold feed for this process to attain a reactor exit temperature of 600 to 650°C. Other factors on which the costs in Table 8.2.2 are based are: the system is installed at the site of the waste generator; the units are owned and operated by the waste disposer; and the units are not equipped with power recovery turbines.

TABLE 8.2.2. MODAR TREATMENT COSTS FOR ORGANIC CONTAMINATED AQUEOUS WASTES

Waste Capacity		Processing Cost[a]	
Gal/day	Ton/day	$/gal	$/ton
5,000	20	\$0.75 - \$2.00	\$180 - \$480
10,000	40	\$0.50 - \$0.90	\$120 - \$216
20,000	80	\$0.36 - \$0.62	\$ 86 - \$149
30,000	120	\$0.32 - \$0.58	\$ 77 - \$139

[a] Based upon an aqueous waste with 1800 BTU/lb heating value (equivalent to a 10% organic waste). Does not include energy recovery value of approximately \$0.05 per gallon

Source: Reference 6

If the waste has a fuel value of greater than 1,800 Btu/lb, the cost will be higher per unit of waste processed. In treating a waste with a higher organic content, it is recommended that the waste is diluted to a 10 percent benzene-equivalent. Therefore, the increase in cost will be in proportion to the increase in organic content.

If the waste has a heat content of between 5 and 10 percent benzene-equivalent, fuel can be added to the waste to bring the heat content up to 10 percent benzene-equivalent without appreciable cost increases. If, however, the waste is very dilute (2 to 3 percent benzene-equivalent), it is more economical to use a combination of fuel with regenerative heat exchange.

8.2.4 Overall Status of Process

8.2.4.1 Availability--

A pilot plant with capacity to oxidize 30 gal/day of benzene equivalent has been in operation at MODAR's laboratory as well as at a field site since late 1984. As a result of these activities, the MODAR SCW oxidation process has been declared commercial and design of the first plant is underway. The plant will be installed late in 1987 and will treat 10,000 to 30,000 gallons of aqueous waste per day.

8.2.4.2 Application--

SCW oxidation would appear to be applicable to aqueous wastes containing 1 to 20 weight percent organics. As noted in previous discussions above, complete destruction of all organic solvents/ignitables can be anticipated on the basis of evidence presented by the developer. The high efficiency of destruction can be related to the unique and stringent conditions associated with SCW oxidation which unites oxygen and organic contaminants under relatively high temperatures and pressures.

Restrictive waste characteristics have not been identified in the literature as a problem. The effect of heteroatoms and their reaction products can be anticipated and steps taken to essentially eliminate any deleterious impacts. However, the applicability of solid content wastes to SCW oxidation systems may be problematical. The effectiveness of removal of precipitated inorganic salts by the mechanical separators proposed for the MODAR system may also be a problem. In the absence of particle size and flow and design data it is difficult to predict mechanical separator performance, although separation should be enhanced under the low density SCW conditions. If particles are present, abrasion problems could occur both within the oxidation system and in any subsequent system designed to recover energy from the treated stream.

Supercritical fluid technology is also being considered for a number of applications other than that concerned with the destruction of organic wastes, e.g., supercritical fluid extractions, including the extraction of adsorbed components from granular activated carbon. Fluids such as CO_2, ethane, and ethylene can be used at critical temperature and pressure conditions which are much less severe than those of SCW.[1] However, no data were found which relates the performance of such systems to the extraction of solvent from wastes.

8.2.4.3 Environmental Impacts--

Liquid, solid, and gaseous emissions are generated from the SCW oxidation process. Gaseous emissions consist primarily of carbon dioxide with smaller amounts of oxygen and nitrogen gas. Effluent gas cleaning is not required. N_2O is the most abundant nitrogen oxide in the atmosphere. It does not appear to interact with the nitrogen dioxide photolytic cycle. Any N_2O which might be in the gaseous effluent is not classified as an atmospheric pollutant.

Solid emissions consist of the precipitated inorganic salts. If chlorine compounds are processed, chloride salts are formed, and similarly sulfur is converted to sulfates, and phosphorous to phosphates.[2]

Liquid effluents consist of a purified water stream. Although no data are available for solvent contaminants, six nines destruction has been measured for dioxins. On the basis of these data it is anticipated that solvents of concern will be found only at the ppb level.

8.2.4.4 Advantages and Limitations--

The developer states that the MODAR process for supercritical water oxidation of organics is an improvement in:

- enhanced solubility of gases including oxygen and air in water, which eliminates two-phase flow;
- rapid oxidation of organics, which approaches adiabatic conditions as well as high outlet temperatures, and very short residence times;
- complete oxidation of organics, which eliminates the need for auxiliary offgas processing;
- removal of inorganic constituents, which precipitate out of the reactor effluent at temperatures above 450°C (840°F); and
- recovery of the heat of combustion in the form of supercritical water, which can be a source of high-temperature process heat.[9]

The above advantages are generally relative to the wet air oxidation process which could be considered as an alternative technology to SCW oxidation. The limitations of the process have yet to be determined through commercial operation. Potential limitations relate to cost and equipment limitations due to the stringent temperature and pressure requirements.

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8.3 OZONATION

Chemical oxidation has the potential for removing from wastewaters organic materials which are resistant to other treatment methods, e.g., refractory materials which are toxic to biological systems. Ozone (O_3) is one of the strongest oxidants available, as shown in Table 8.3.1, which lists the oxidation potential and relative oxidation power of a number of oxidizing agents. Ozone, as an oxidant, is sufficiently strong to break many carbon-carbon bonds and even to cleave aromatic ring systems. Oxidation of organic species to carbon dioxide, water, etc., is not improbable if ozone dosage and contact times are sufficiently high, although many compounds are highly resistant to ozone degradation. These compounds, which include oxalic and acetic acids, ketones, and chlorinated organics, are not affected significantly by treatment conditions (1 to 10 mg/liter concentration levels and 5 to 10 minutes contact times) normally used for treating drinking waters or for disinfecting wastewaters.[3]

Ozone has been used for years in Europe to purify, deodorize, and disinfect drinking water. More recently, it has been used in the waste treatment area to oxidize phenolic and cyanide wastewaters. Cost considerations and mass transfer factors limit the use of ozonation to applications involving 1 percent or lower contaminant concentration levels. Since oxidation by ozone occurs nonselectively, it is also generally used only for aqueous wastes which contain a high proportion of hazardous constituitents versus nonhazardous oxidizable compounds, thus focusing ozone usage on contaminants of concern. Ozonation may be particularly useful as a final treatment for waste streams which are dilute in oxidizable contaminants, but which do not quite meet effluent standards.

8.3.1 Process Description

Ozone is generated on site by the use of corona discharge technology. Electrons within the corona discharge split the oxygen-oxygen double bonds upon impact with oxygen molecules. The two oxygen atoms formed from the molecule react with other oxygen molecules to form the gas ozone, at equilibrium concentration levels of roughly 2 percent in air and 3 percent in oxygen (maximum values of 4 and 8 percent, respectively). Ozone must be

TABLE 8.3.1. RELATIVE OXIDATION POWER OF OXIDIZING SPECIES

Species	Oxidation potential, volts	Relative oxidation power[a]
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radicals	1.70	1.25
Permanganate	1.70	1.25
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00

[a] Based on chlorine as reference (= 1.00)

Source: References 1 and 2.

produced onsite (ozone decomposes in a matter of hours to simple, molecular oxygen[4]) and ozonation is restricted to treatment of streams with low quantities of oxidizable materials. Using a rule of thumb, two parts of ozone are required per pound of contaminant. A large commercial ozone generator producing 500 lb/day of ozone could treat 1 million gallons/day of wastewater containing 30 ppm of oxidizable matter, or equivalently, 3,000 gallons/day of wastewater containing 1 percent of oxidizable matter.[2] Extensive information related to the generation of ozone and its application to the treatment of industrial wastewaters can be found in References 5 through 9.

While direct ozonation of industrial wastewater is possible and is practiced commercially, other technologies have been combined with ozonation to enhance the efficiency and rate of the oxidation reactions. These technologies, which supply additional energy to the reactants, involve the use of ultraviolet light or ultrasonics. In all cases it is important that mass transfer across the gas-liquid interface with one or more of the reactants be facilitated to maximize reaction rates.

8.3.1.1 Pretreatment Requirements--

Due to the nonselective nature of the ozonation reactions it is important that the concentration levels of nonhazardous, but oxidizable, contaminants in the feed stream be reduced as much as possible prior to treatment. The strong electrophilic nature of ozone imparts to it the ability to react with a wide variety of organic functional groups, including aliphatic and aromatic carbon-carbon double and triple bonds, alcohols, organometallic functional groups, and some carbon-chlorine bonds. It is important to recognize that many functional groups can be present which compete for the ozone reactant and can add significantly to the cost of the treatment.

The waste to be treated should also be relatively free of suspended solids, since a high concentration of suspended solids can foul the equipment normally used to bring about contact between ozone and the aqueous phase contaminants. When ozonation is combined with UV radiation or ultrasonics, a high concentration of suspended solids also can impede the passage of UV radiation or attenuate the energy supplied by ultrasonics to enhance the oxidation rate.

8.3.1.2 Operating Parameters--

To effectively bring about the reaction of ozone with reactive contaminants, it is important that mass transfer of ozone and its reactants through the gas-liquid interface be maximized. Also, to increase ozone solubility in water, temperatures should be maintained as low as possible and pressures as high as possible. However, conditions such as high temperature, high pH, and high UV light flux favor ozone decomposition. Under these conditions reactivity rates may increase, although costs may also increase due to less efficient use of ozone. Decisions will have to be made on a case-by-case basis to establish the most effective operating conditions.

Several commercial designs are available for the conduct of gas/liquid reactions which bring reactants into contact as effectively as possible. The types of reactor designs available range from mechnically agitated reactors to more complex spray, packed, and tray type towers. Their advantages and limitations are discussed in detail in many standard texts and publications (for example, see References 2 through 5).

The process of UV/ozone treatment operates in the following manner. The influent to the system is mixed with ozone and then enters a reaction chamber where it flows past numerous ultraviolet lamps as it travels through the chamber (use Figure 8.3.1). Flow patterns and configurations are designed to maximize exposure of the total volume of ozone-bearing wastewater to the high energy UV radiation. Although the nature of the effect appears to be influenced by the characteristics of the waste, the UV radiation enhances oxidation by direct dissociation of the contaminant molecule or through excitation of the various species within the waste stream. In industrial systems, the system is generally equipped with recycle capacity. Gases from the reactor are passed through a catalyst unit, destroying any volatiles, replenished with ozone, and then recycled back into the reactor. The system has no gas emissions.

Another alternative process involves the coupling of ultrasonic energy with ozonation. It has been shown that significant increases in the rate of oxidation can be obtained by the use of ultrasonic energy as opposed to ozone alone. Experimental details were not available in Reference 3, although different oxidation pathways were reported operating in the presence or absence of untrasonics.

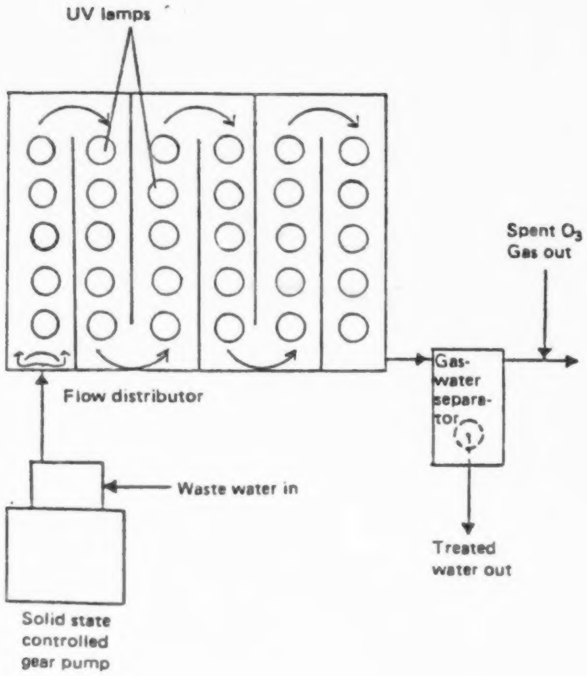

Figure 8.3.1. Schematic of top view of ULTROX pilot plant by General Electric (ozone sparging system omitted) (Edwards, B.H., 1983).

Source: Reference 4.

Regardless of the reaction mechanisms, there appears to be no doubt that the combination of ozonation with either UV or ultrasonic excitation leads to increased oxidation rates. Typical design data for a 40,000 gal/day UV/ozone treatment process are shown in Table 8.3.2. The plant is designed to reduce a 50 ppm PCB feed concentration to a 1 ppm effluent.

As noted, both temperature and pH can have a significant effect on the rate of ozonation. As an example, work reported in Reference 11 indicates that the reaction rate of toluene in acidic solutions with pH values of 2 and 3, increases by a factor of two for a temperature increase of 10°C. In neutral solutions, however, the rate increases about ten times for the same temperature change of 10°C. The activation energies were calculated to be 11.22 kcal/g mole and 31.26 kcal/g mole respectively, for the acidic and neutral conditions. Thus, the data show that the ozonation rate of toluene increases with increasing temperature and decreasing acidity of the solution.

8.3.1.3 Post-Treatment Requirements--

Post-treatment of industrial wastewaters that have been contacted with ozone will involve elimination of residual ozone, usually by passing the effluent through a thermocatalytic unit. Some by-product residuals may be formed in the feed water and some contaminants, if present, will not undergo reaction. Compounds considered unreactive include many chlorinated aliphatic compounds. If these compounds are present in the waste, technologies other than ozonation should be considered.

8.3.1.4 Treatment Combinations--

Apart from the employment of UV excitation and ultrasonics with the ozonation process, ozonation can be considered as a finishing step for waste streams which have been treated by other technologies, principally biotreatment systems. It has also been tested with some success as a means of enhancing biotreatability. Although the use of ozonation in combination with other technologies such as biological treatment is a possible solvent waste treatment alternative, it is not a demonstrated technology for industrial wastewaters, despite its extensive use and success in treating and disinfecting relatively clean drinking waters.

TABLE 8.3.2. DESIGN DATA FOR A 40,000 GPD (151,400 L/DAY) ULTROX PLANT

Reactor	
Dimensions:	
Meters (LxWxH)	2.5 x 4.9 x 1.5
Wet volume, liters	14,951
UV lamps:	
Number of 65 watt lamps	378
Total power, KW	25
Ozone Generator	
Dimensions:	
Meters (LxWxH)	1.7 x 1.8 x 1.2
gms ozone/minute	5.3
kg ozone/day	7.7
Total power, kW	7.0
Total energy required (KWH/day)	768

Source: Reference 10.

8.3.2 Demonstrated Performance

Data for the treatment by ozonation of contaminated solvents and other low molecular weight organics wastes are sparse. However, relative activities for several solvents and other low molecular weight organic compounds are shown in Table 8.3.3. As noted, chlorinated aliphatics must be considered nonreactive.

Another study[12] of the ozonation of petrochemical waste streams concluded that ozonation was feasible for complete oxidation of only one of four waste streams studied. This was a stripped ethylene dichloride (EDC) wastewater. Waste streams deemed unsuitable for treatment by ozonation were streams from the manufacture of toluene diisocyanate, ethylene glycol, and styrene. TOC destruction within the EDC stream was 82 percent of a 100 mg/L feedstream TOC level after 3 hours reaction time. A weight ratio of ozone to TOC of 5.6 was required to achieve total oxidation. Ozone/TOC weight ratios were higher for the streams deemed not suitable for ozonation. However, an improvement in biotreatability was noted for all streams.

In the case of UV-assisted ozonation, a California study[13] reported that trichloroethylene concentrations were reduced from 17 ppb to less than 0.1 ppb. Similar results were attributed to ultrasonic energy used in place of UV radiation. Reference was also made to a UV ozone treatment system being operated by Boeing to treat methylene chloride in water at the 4,000 mg/kg concentration level.

8.3.3 Cost of Treatment

Table 8.3.4 lists the costs for a 40,000 GPD UV/Ozone plant for which design data were shown in Table 8.3.2.. Cost estimates were based on wastewater containing 50 ppm PCB, designed to achieve an effluent PCB concentration of 1 ppm. Costs were considered to be competitive with activated carbon. The unit cost for treatment of the waste is greatly affected by whether or not the cost for a monitoring system is included. The cost of PCB destroyed is in excess of $10/pound. PCB data were used for costing purposes because of its availability. However, the costs will increase substantially if ozonation is to be used as treatment for a waste containing 1 percent organic contaminants. This is 200 times the

TABLE 8.3.3. OZONATION TREATMENT OF SOLVENTS AND IGNITABLES

Compound	Relative reactivity with ozone	Oxidation products
Priority Solvents		
carbon tetrachloride	unreactive	
chlorobenzene	intermediate	CO_2, oxalic acid,Cl^-, o-, m- & p-chlorophenols and chlorotartaric acid
p-cresol (p-methylphenol)	fast; 21.67 mg/L - no aromaticity after 17 min. ozonation	
o-dichlorobenzene	100 mg/L - 95% destroyed in 15 min.; 100% destroyed in 30 min. with UV/O_3	
methyl ethyl ketone	very slow with O_3; fast with UV/O_3	acetone, ethanol and acetate
nitrobenzene	fast with UV/O_3/ intermediate with ozone alone	o-, m- & p-nitriphenols (mostly p-); all CO_2 after 50 min. UV/O_3; only oxalic acid with ozone alone
pyridine	unreactive at low pH	
tetrachloroethylene	unreactive	
toluene	intermediate	CO_2, OCOOH, oxalic acid
trichloroethylene	very slow	
trichlorofluoromethane	unreactive	
xylenes (o-, m-, p-)	fast	CO_2, OCOOH, oxalic acid

(continued)

TABLE 8.3.3 (continued)

Compound	Relative reactivity with ozone	Oxidation products
Other Solvents		
acetonitrile	probably fast	probably HOAc and NO_3^-
bis(chloromethyl)ether	unreactive	
benzene	slow	CO_2, oxalic acid
chloroform	unreactive to ozone but stripped	Cl^-, probably $COCl_2$ (phosgene) and CO_2; from solution; reactive with ozone/UV 25% of theoretical Cl^- after 2 hrs. of UV/ozonation
dichlorodifluoromethane	unreactive	
1,1-dichloroethane	unreactive	
1,2-dichloroethane	unreactive	
1,1-dichloroethylene	fast	
1,2-dichloroethylene	fast	
hexachloroethane	unreactive	
1,1,1,2-tetrachloroethane	unreactive	
1,1,2,2-tetrachloroethane	unreactive	
1,1,2-trichloroethane	unreactive	

(continued)

TABLE 8.3.3 (continued)

Compound	Relative reactivity with ozone	Oxidation products
Ignitables		
acetaldehyde	fast	CH_3COOH
allyl alcohol	probably fast	probably HCHO and $HOCH_2COOH$
chloroacetaldehyde	intermediate	$ClCH_2COOH$
formaldehyde	fast	formic acid, then CO_2

Source: Reference 3

TABLE 8.3.4. EQUIPMENT PLUS OPERATING AND MAINTENANCE COSTS; 40,000 GPD UV/OZONE PLANT

Reactor	$ 94,500
Generator	30,000
	$124,500
O & M Costs/Day	
Ozone generator power	$4.25
UV lamp power	15.00
Maintenance (Lamp Replacement)	27.00
Equipment Amortization (10 years @ 10%)	41.90
Monitoring labor	85.71
TOTAL/DAY	$173.86
Cost per 1,000 gals (3,785 liters) with monitoring labor	$4.35
Cost per 1,000 gals without monitoring labor	$2.20

Source: Reference 10.

concentration used to develop the costs in Table 8.3.4 Assuming capital equipment costs follow a simple "sixth-tenths" factor scaling relationship, the costs of the reactor and generator would be about $3,000,000 (or 24 times the costs shown in Table 8.3.4) for treatment of this higher concentration. Scale factors would be variable for the operating and maintenance cost items listed in Table 8.3.4. However, the net result of scale-up to handle the more concentrated waste would drastically increase the cost/1,000 gallons treated, but would also result in far lower costs when calculated on the basis of the amount of contaminant destroyed. Costs of roughly $10/pound of contaminant destroyed would be reduced to an estimated $1/pound, assuming comparable efficiencies. Destruction efficiencies may be adversly affected at higher concentrations due to mass-transfer and other considerations. Thus, the cost benefits per pound of contaminant destroyed, as stated above, may not be fully achievable. Ozone usage and the corresponding costs are dependent on the concentration of oxidizable species in the waste stream. The amount of UV radiation used depends on quantum yield which can vary widely depending upon waste characteristics and process condition. An optimal tradeoff must be made on the basis of pilot-scale or full scale test results.

8.3.4 Overall Status of Process

8.3.4.1 Availability--

Ozonation equipment is available commercially from several manufacturers within the United States. The Chemical Engineers' Equipment Guide published by McGraw Hill lists nine manufacturers of ozone generators and 10 manufacturers of ozonators. The latter classification includes firms that usually provide the ozone generator, the reactor, and auxiliaries such as the catalytic unit for destruction of ozone from the treated stream. The status of UV/ozonation is far less advanced. Processes such as the Ultrox process[4] have been concerned with highly refractory compounds such as PCBs. Equipment specifically designed and available for UV/ozonation of industrial wastewaters, is not available as a standard commercial item.

8.3.4.2 Application--

Ozonation generally cannot be used as a sole treatment technology for wastes which are resistant to oxidation such as chlorinated aliphatic hydrocarbon wastes, and for those wastes containing solvent contaminants which form stable intermediates that are resistant to total oxidation. Ozonation appears best suited for treatment of very dilute waste streams, similar to those streams treated by the ozone based water disinfection processes now used in Europe. It does not appear to be cost competitive or technically viable for most industrial waste streams where organic concentration levels are 1 percent or higher. However, it may be viable for certain specific wastes with high levels of a contaminant of special concern and high reactivity.

8.3.4.3 Environmental Impact--

Assuming adequate destruction of a contaminant by ozonation, the principal environmental impact would appear to be associated with ozone in the effluent vapor and liquid streams. However, thermal decomposition of ozone is effective and is used commercially to destroy ozone prior to discharge. Unreacted contaminants or partially oxidized residuals in the aqueous effluent may be a problem necessitating further treatment by other technologies. Presence of many such residuals will generally result in selection of a more suitable alternative technology.

8.3.4.4 Advantages and Limitations--

There are several factors which suggest that ozonation may be a viable technology for treating certain dilute aqueous waste streams:[1,4]

- Capital and operating costs are not excessive when compared to incineration provided oxidizable contaminant concentration levels are less than 1 percent.
- The system is readily adaptable to the onsite treatment of hazardous waste because the ozone can and must be generated onsite.
- Ozonation can be used as a final treatment for certain wastes since effluent discharge standards can be met.
- It can be used as a preliminary treatment for certain wastes.(e.g., preceeding biological treatment).

However, there are limitations which often will preclude use of ozonation as a treatment technology. These include:

- Ozone is a nonselective oxidant; the waste stream should contain primarily the contaminants of interest.
- Certain compounds because of their structure are not amenable to ozonation,e.g., chlorinated aliphatics.
- Ozone systems are generally restricted to 1 percent or lower levels of toxic compounds. The system is not amenable to bulky wastes.
- Toxic intermediates may persist in the waste stream effluent.
- Ozone decomposes rapidly with increasing temperature, therefore, excess heat must be removed rapidly.

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8.4 OTHER CHEMICAL OXIDATION PROCESSES

Chemical oxidation processes are potential options for the treatment of hazardous organic wastes, including those containing solvent and ignitables. Previously described oxidation processes such as wet air oxidation and supercritical water oxidation can be considered to be a type of incineration, since the ultimate reaction products of most organic constituents treated by those processes are carbon monoxide and water. Other oxidation processes, including the ozonation process described in section 8.3, generally do not result in total destruction of organic waste constituents. They are processes which are carried out at ambient or moderate conditions of temperature and pressure, and except for a small number of readily oxidizable compounds, or in cases where an activator such as ultraviolet light is used, residual contaminants and oxidation resistant by-products remain after treatment. These residuals will generally require additional processing. Thus, the chemical oxidation processes described here are considered pretreatment processes for compounds in aqueous wastes at the one percent or lower level. They can also be used as a finishing or polishing step for very dilute waste streams containing contaminants which are known to be amenable to treatment. The specific features and applications of other oxidizing agents such as hydrogen peroxide and potassium permanganates are discussed here. As shown in Table 8.4.1, these compounds are relatively powerful oxidizing agents as illustrated by their high oxidation potentials.

8.4.1 Process Description

As shown in Table 8.4.1, hydrogen peroxide, H_2O_2, and potassium permanganate, $KMnO_4$, are both relatively strong oxidizing agents. Hydrogen peroxide has been used to treat phenols, cyanides, sulfur compounds, and metal ions in dilute waste streams. Potassium permanganate is primarily used in the treatment of phenols. The choice of oxidant is dependent upon such factors as toxicity, reaction rate, ease of removal of secondary products, simplicity and cost.

TABLE 8.4.1. RELATIVE OXIDATION POWER OF OXIDIZING SPECIES

Species	Oxidation Potential, volts	Relative Oxidation Power*
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radicals	1.70	1.25
Permanganate	1.70	1.25
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00

*Based on chlorine as reference (= 1.00).

Source: References 1 and 2.

Oxidation with H_2O_2 is generally performed in the presence of a metal catalyst. Typical catalysts include ferrous sulfate, iron wool, nickel salts, and aluminum salts. The waste is heated and then treated with H_2O_2 while being agitated. The H_2O_2 oxidation tends to proceed quickly under basic conditions.[3] The feasibility of ultraviolet catalyzed H_2O_2 oxidation has been studied, but it does not appear to be used on an industrial scale.[4]

Potassium permanganate oxidation is favored under basic conditions. Raising the pH to the optimum level is accomplished by the addition of lime, soda ash, or caustic soda. Potassium permanganate has also been used in the treatment of aldehydes, mercaptans, and unsaturated acids.[3] A schematic of a typical process utilizing pH modification is shown in Figure 8.4.1.[5]

8.4.1.1 Pretreatment Requirements for Different Waste Forms and Characteristics--

Possible pretreatment required, prior to oxidation with either H_2O_2 or $KMnO_4$, is filtration to remove oxidizable solids from the waste stream. This is necessary since these oxidizing agents are not selective in their reaction with waste constituents.

As noted in Reference 6, chemical oxidation is best suited for aqueous liquids containing less than one percent of the oxidizable compound. Violent reactions may occur when oxidizing agents are added to significantly higher concentrations of easily oxidizable organics. Strong oxidants are relatively nonselective; therefore, any easily oxidizable material will react. In a very qualitative way, the reactivity of selected organic compounds with respect to oxidation is as follows:

1. High reactivity - phenols, aldehydes, aromatic amines, certain organic sulfur compounds, e.g., thioalcohols, thioethers;
2. Medium reactivity - alcohols, alkyl-substituted aromatics, nitro-substituted aromatics, unsaturated alkyl groups, carbohydrates, aliphatic ketones, acids, esters, and amines; and
3. Low reactivity - halogenated hydrocarbons, saturated aliphatic compounds, benzene.

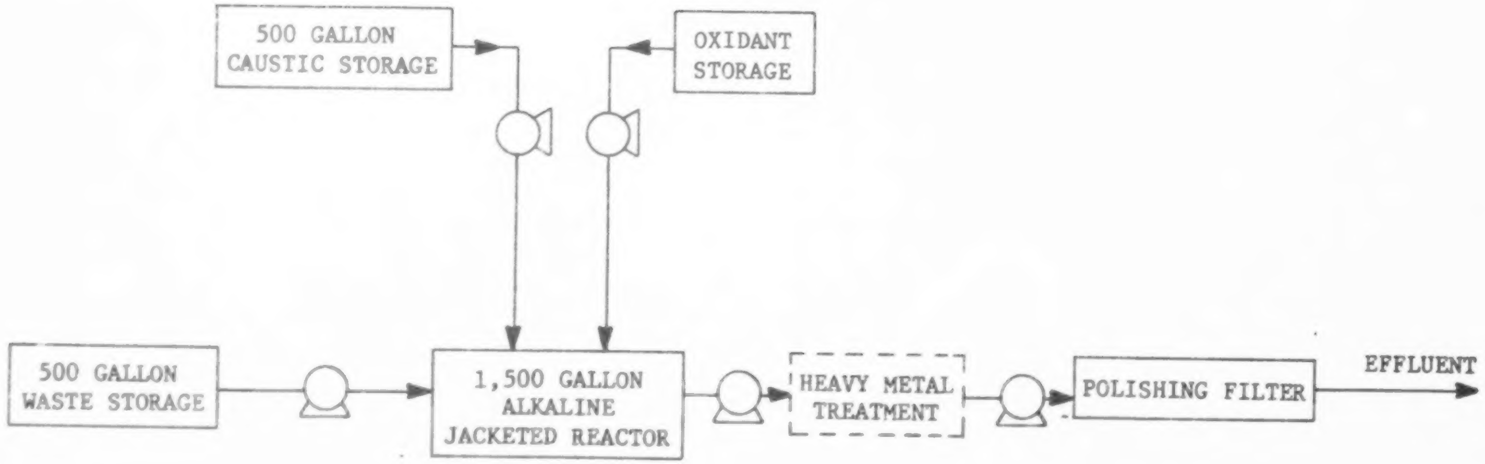


Figure 8.4.1. Example process flowsheet - oxidation.

Source: Reference 5.

Chemical oxidation is not suitable for wastes containing significant amounts of compounds or properties that represent an excessive demand for oxidant, such as BOD, COD, nitrogen, or phosphorus. If the waste matrix to be oxidized contains a significant amount of material that is more easily oxidized than the toxic constituents of concern, then oxidant demand exhibited by the easily oxidized species must be met before oxidation of the constituents of concern will take place. For this reason, oxidation often has limited application to solvent containing sludges.

8.4.1.2 Operating Parameters--

Operating parameters common to the reactivity of most oxidizing agents include temperature and pH. Both H_2O_2 and permanganate work best under elevated temperatures. The optimum pH range for oxidation of phenols by H_2O_2 in the presence of metal catalysts is 3 to 4, while that for $KMnO_4$ increases as pH increases up to a value of 9.5.[7]

In the treatment of phenols, $KMnO_4$ cleaves the aromatic ring and forms a variety of mostly aliphatic acids. The stoichiometric equation indicates that somewhat more than 9 moles of $KMnO_4$ are needed to oxidize each mole of phenol to CO_2. On a weight basis then, 16 parts $KMnO_4$ per part phenol would be required for complete oxidation. However, many applications require only that the phenols be degraded to less toxic acids. In this case, 6 to 7 ppm $KMnO_4$ per ppm phenol is sufficient to achieve 90% phenol removal.[3]

Very simple equipment is required for chemical oxidation. This includes storage vessels for the oxidizing agents and perhaps for the waste, metering equipment for both streams, and vessels with agitators to provide contact between the oxidant and the waste. Some instrumentation is required to determine the concentrations of pollutants, pH, and the degree of completion of the oxidation reaction. The process is usually monitored by an oxidation-reduction (ORD) potential electrode.[5]

8.4.1.3 Post-Treatment Requirements--

As noted, the chemical oxidation processes discussed here often do not result in total destruction of the initial contaminants and their by-products. As a result, further treatment may be necessary to reduce residuals in the treated waste stream to acceptable levels. In addition, some of the residuals generated from chemical oxidation are attributable to the use of additives such as lime, soda ash, or caustic soda used to raise the pH of the waste.

As a result, solids removal is usually necessary prior to discharge or further treatment. Another disadvantage of chemical oxidation for waste treatment is that it can introduce new metal ions into the effluent. Potassium permanganate used to treat wastes will be reduced to MnO_2 in the process. This can be reduced by filtration to levels less than 0.05 mg/l in the final effluent. On the other hand, oxidation by hydrogen peroxide adds no harmful species to the final effluent (except perhaps excess peroxide) since its product is water. However, the reaction of hydrogen peroxide with chlorinated organics in the presence of UV light may create chloride ions, a situation which may call for additional processing.

8.4.2 Demonstrated Performance

A recent study was conducted at the University of Connecticut[4] to investigate the destruction of halogenated aliphatics in water by ultraviolet catalyzed oxidation using H_2O_2 as the oxidant. The effectiveness of this process was determined for typical halogenated aliphatics, including trichloroethylene, tetrachloroethane, dichloromethane, chloroform, carbon tetrachloride and ethylene dibromide. Conventional biological, physical and chemical wastewater treatment methods are often ineffective in removing these types of hazardous compounds. The UV catalyzed H_2O_2 system was investigated as an alternative treatment method to the use of ozone and UV light.

The chemistry of the H_2O_2/UV reaction involves generation of hydroxyl radicals and other reactive species by the photochemical action of UV light on H_2O_2. The hydroxyl radicals attack organic species by extracting a hydrogen atom or by adding to the double bonds of unsaturated molecules. In addition, the UV light may also activate certain organic species and make them more susceptible to attack by hydroxyl radicals. Under suitable operating conditions the final products are CO_2, H_2O, H^+ and Cl^-, if chlorinated organics are in the waste stream.

The destruction of trichloroethylene (TCE) was studied in greatest detail. The concentrations of TCE, initially 58 ppm, and H_2O_2 were followed with time and chloride ion was determined at the beginning and end of each run. The synergistic effect of H_2O_2 plus UV light on the destruction of TCE is shown in Figure 8.4.2. With H_2O_2 and no UV light the reaction rate was negligible. A moderate rate of reaction was achieved when the waste was exposed to UV light with no H_2O_2 present. In the H_2O_2/UV system all of the reacted chlorine was converted to chloride ions, showing that no other chlorinated organics were formed.

Other factors studied were the effect of increasing the initial concentration of contaminant, increasing the amount of H_2O_2 used, increasing the temperature in the reaction vessel, and increasing the pH. Doubling the initial concentration of TCE decreased the rate of oxidation although low levels of TCE were still achieved. The rate of reaction increased with increasing initial concentration of H_2O_2, probably as a result of higher concentrations of hydroxyl radicals. The time needed to reach any specified TCE level was approximately halved by each 10°C temperature increase. However, the faster reaction rate was achieved at the expense of larger peroxide consumption. The rate of reaction increased with increasing pH over the range of 5.5 to 7.9, but the effect of pH was minimal.

The variables studied for the six remaining compounds were temperature and the presence or absence of H_2O_2. As with TCE, there was a strong synergistic effect when the compounds were exposed to both H_2O_2 and UV light. However, the presence of H_2O_2 had a lesser effect on the destruction of the other compounds. Temperature had a significant effect on the rate of reaction for all compounds. Figure 8.4.3 compares the rate of reactions for the compounds studied at 20°C and 30°C, respectively.

8.4.3 Cost of Treatment

Since H_2O_2 and $KMnO_4$ are not used on an industrial scale to treat organic wastes, cost data were not available. However, in comparing H_2O_2/UV treatment to ozone/UV treatment, it is clear that the former may be more economically attractive because:[4]

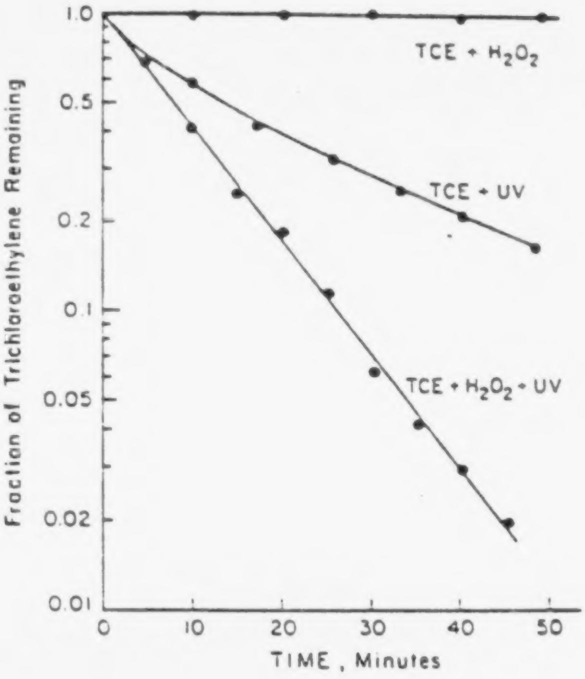
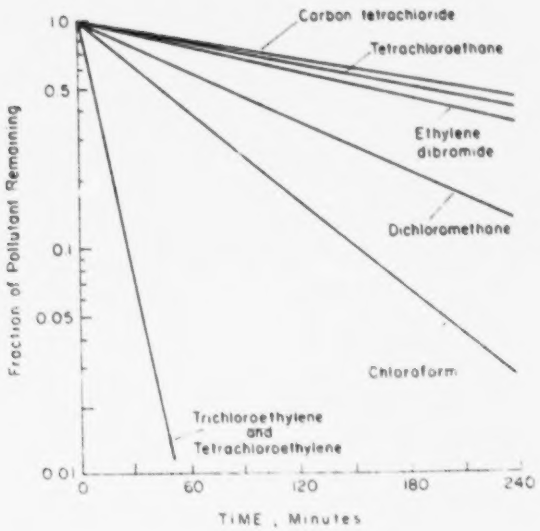
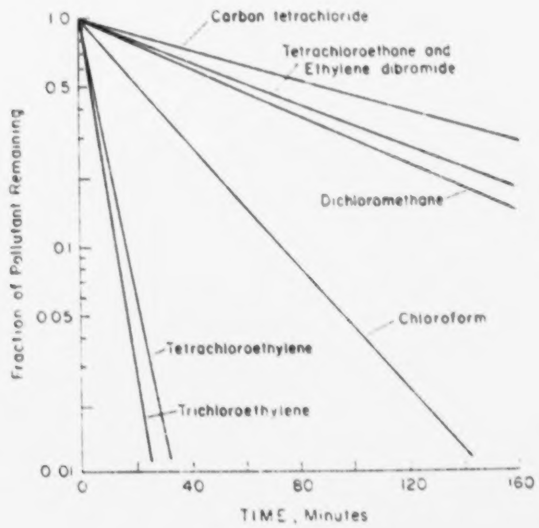


Figure 8.4.2. Effect of H_2O_2 alone, UV alone, and H_2O plus UV on decomposition of trichloroethylene (TCE) at 20°C, pH 6.8. Initial TCE = 58 ppm. Initial H_2O_2/TCE = 4.5 mols/mol.



Comparison of rates of reaction of halogenated aliphatics at 20°C.



Comparison of rates of reaction of halogenated aliphatics at 30°C.

Figure 8.4.3. Rates of reaction of halogenated aliphatics at 20°C and 30°C.

- The cost of H_2O_2 is much less sensitive to the scale of operation than ozone.
- H_2O_2 can be stored for use on an intermittent basis according to process demand.
- The H_2O_2 solution can be ready mixed with wastewater, whereas ozone gas must be transferred into the water by mass transfer from the ozone gas.

Both oxidants are currently used in the treatment of phenols, so it can be inferred that they are capable of destructing aromatics. Whether they are able to treat aromatic solvents or ignitables has not been demonstrated.

8.4.4 Overall Status of Process

8.4.4.1 Availability/Application--

Technology for large-scale applications of chemical oxidation is well developed and equipment requirements are straightforward and simple. Application to industrial wastes is well developed for cyanides and for other hazardous species in dilute waste streams (phenols, organic sulfur compounds, etc.). Oxidation has limited application to slurries, tars, and sludges. because other components of the sludge, as well as the material to be oxidized, may be attacked indiscriminately by oxidizing agents; careful control of the treatment via multistaging of the reaction, careful control of pH, etc., are required.

The application of oxidation processes to the solvents and ignitables of direct concern has not yet been established. Some level of destruction can be expected but full destruction has generally not been realized except possibly in the Reference 4 study. This study, performed at the University of Connecticut, clearly showed that the H_2O_2/UV process is capable of treating organic compounds, specifically halogenated aliphatics and particularly the unsaturated chlorinated compounds. Apparently the hydroxyl radicals and other reactive species generated by UV radiation attack the double bonds more readily. Similar studies need to be performed for $KMnO_4$.

8.4.4.2 Environmental Impacts--

The environmental impact of the processes discussed here relate to the unreacted contaminants and by-products remaining in the waste stream. Additional treatment usually will be required. Air emissions associated with the use of hydrogen peroxide and permanganate oxidants will be minimal, although some care must always be observed when the contaminants are high vapor pressure solvents and ignitables.

8.4.4.3 Advantages and Limitations--

The advantages of the oxidation processes discussed here result from ease and simplicity of operation. Disadvantages are the result of incomplete destruction and the need for subsequent treatment of the oxidized waste stream.

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8.5 CHLORINOLYSIS PROCESSES

8.5.1 Process Description

Chlorine is a strong oxidizing agent and is often used in much the same manner as other oxidants (e.g., ozone, hydrogen peroxide, and potassium permanganates) to treat low levels of organic contaminants in aqueous waste streams. However, in the process termed chloronolysis (or chlorolysis in Germany), chloride is introduced to the waste at high temperatures and pressures. At temperatures above 500°C, under excess chlorine conditions, the carbon-carbon bonds of hydrocarbons can be broken and the molecular fragments can react with chlorine to form low molecular weight chlorinated hydrocarbons. It is essentially a pyrolytic process carried out in the presence of chlorine. Typical chlorinolysis reactions are shown in Table 8.5.1. As shown in the table, the mole ratio of HCl to carbon tetrachloride (CCl_4) produced varies from zero to two. This ratio can be compared to a ratio of four for the process based on the direct chlorination of methane, and will generally impact favorably on subsequent purification and disposal operations required by the two processes.

Several companies have developed manufacturing processes that are capable of converting C_1, C_2, and C_3 hydrocarbons and their partially chlorinated derivatives to chlorinated solvents such as trichloroethylene, perchloroethylene, and carbon tetrachloride.[2] Another company, Hoechst-Uhde, has patented a process in Germany for converting C_1 to C_6 organochlorine compounds to carbon tetrachloride. The operating characteristics of the four chlorinolysis processes are summarized in Table 8.5.2.[2,3]

The Hoechst-Uhde process is the only chlorinolysis process which appears capable of handling aromatic feedstocks. The higher reactor temperatures (600°C) and pressures (20 MPa) used in the Hoechst-Uhde process apparently promote the breakdown of the benzene ring. Two of the other processes operate at temperatures around 400°C, and at this temperature are not capable of destroying hexachlorobenzene which is formed as a breakdown product of the benzene ring.[4] The third American process, although it reportedly operates at 600°C, does not bring about destruction of the hexachlorobenzene, probably because of less stringent pressure conditions.

TABLE 8.5.1. TYPICAL CHLORINOLYSIS REACTIONS

Organic feedstock	Process	Enthalpy, $\Delta H^{\circ}_{\rightarrow}$298°K,kcal/mole	Mole ratio, HCl/CCl_4
Hexachloroethane	$CCl_3\text{-}CCL_3+Cl_2 \rightarrow 2CCl_4$	15	0
1,2-dichloroethane	$CH_2Cl\text{-}CH_2Cl+5Cl_2 \rightarrow 2CCl_4+4HCl$	106	2
1,2-dichlorobutane	$CH_2CL\text{-}CHCl\text{-}CH_3+8Cl_2 \rightarrow 3CCl_4+6HCl$	142	2
Hexachlorobutadiene	$CCl_2{=}CCl\text{-}CCl{=}CCl_2+5Cl_2 \rightarrow 4CCl_4$	96	0
Benzene	$C_6H_6+15Cl_2 \rightarrow 6CCl_4+6HCl$	300	1
Hexachlorobenzene	$C_6Cl_6+9Cl_2 \rightarrow 6CCl_4$	140	0

Source: Reference 1.

TABLE 8.5.2. OPERATING CHARACTERISTICS OF CHLORINOLYSIS PROCESSES

Process Developer	Feedstock	Operating Conditions	Product Yield	Comments
Dow Chemical	C_1, C_2, C_3 hydrocarbon products & their partially chlorinated derivatives.	600°C	94-95% of perchloroethylene and carbon tetrachloride, 6% of hexachlorobenzene.	Hexachlorobenzene is one of the hard to treat wastes.
Diamond Alkali	Ethylene dichloride.	400°C, using Fuller's earth as catalyst in fluid bed	90% yield of perchloroethylene and trichloroethylene; the balance estimated to be hexachloroethane, hexachlorobutadiene, hexachlorobenzene, tetrachloroethane, pentachloroethane.	The tetrachloroethane & pentachloroethane can be recycled and pyrolized to trichloroethylene. The hexachlorobutadiene & hexachlorobenzene are expected to be residues from this process.
Pittsburgh Plate Glass	Ethylene dichloride and other C_2 chlorohydrocarbons.	400°C, oxychlorination in a fluid bed catalytic reactor	85% yield of trichloroethylene and perchloroethylene; the balance probably carbon oxides, and chlorohydrocarbons such as hexachlorobutadiene and hexachlorobenzene.	Relatively low yield to useful products. The hexachlorobutadiene and hexachlorobenzene formed are expected to be residues from this process.
Hoechst Uhde	C_1 to C_6 organochlorine compounds.	600°C and 20 MPa	>95% yield of carbon tetrachloride per pass. Heavy ends consist chiefly of hexachlorobenzene.	Very high overall yield to carbon tetrachloride if the presence of oxygenated chlorohydrocarbons in the feedstocks is limited. The hexachlorobenzene formed can be recycled to extinction.

Source: References 2 and 3.

A schematic of the Hoechst-Uhde process is shown in Figure 8.5.1. The organic feedstock and preheated chlorine are introduced into a high purity seamless nickel tube reactor which is surrounded by a stainless steel jacket to withstand the 20 MPa pressures. In the primary section of the reactor, the feed is heated and the reaction is initiated. Since the reaction is exothermic, the electric heaters can be turned off after initiation, and the reaction is allowed to proceed to an adiabatic end temperature of 620°C. The final temperature is regulated by chlorine addition which must be 20 percent in excess of theoretical, and is normally maintained at 50 percent in excess of theoretical.[1] Quenching from 620°C to 500°C takes place in the final section of the reactor by injection of cold carbon tetrachloride bled from the output stream.[3]

The remainder of the process consists of distillation columns where reaction products are separated, resulting in CCl_4 and HCl streams, and also a waste stream consisting of phosgene (from oxygen-bearing organics), and chlorine.

As noted in Reference 1, in principle any liquid chlorinated hydrocarbon mixture can be used as a feedstock for the Hoechst process. Suitable feedstocks include residues from the production of vinyl chloride monomer, chloromethanes, propylene oxide, allyl chloride, perchloroethylene and benzene chlorination.[3] Other wastes which have been considered as feedstocks for chlorinolysis are pesticide wastes. Of 20 pesticides considered, however, only 13 contain the desirable elements: carbon, hydrogen and chlorine. These include aldrin, chlordane, DDT, ethylene dichloride, benzene hexachloride, heptachlor, landane, o- and p-dichlorobenzene, and perthane. In a previous study, it was determined that nine of these compounds are manufactured in too low a volume (1 MM lb/yr) to be considered as significant feedstocks. Three others, aldrin, chlordane, and DDT were produced in large volumes, but have since been banned by the EPA. The conclusions of the study were that the pesticides industry did not produce significant quantities of waste suitable for chlorinolysis.[2]

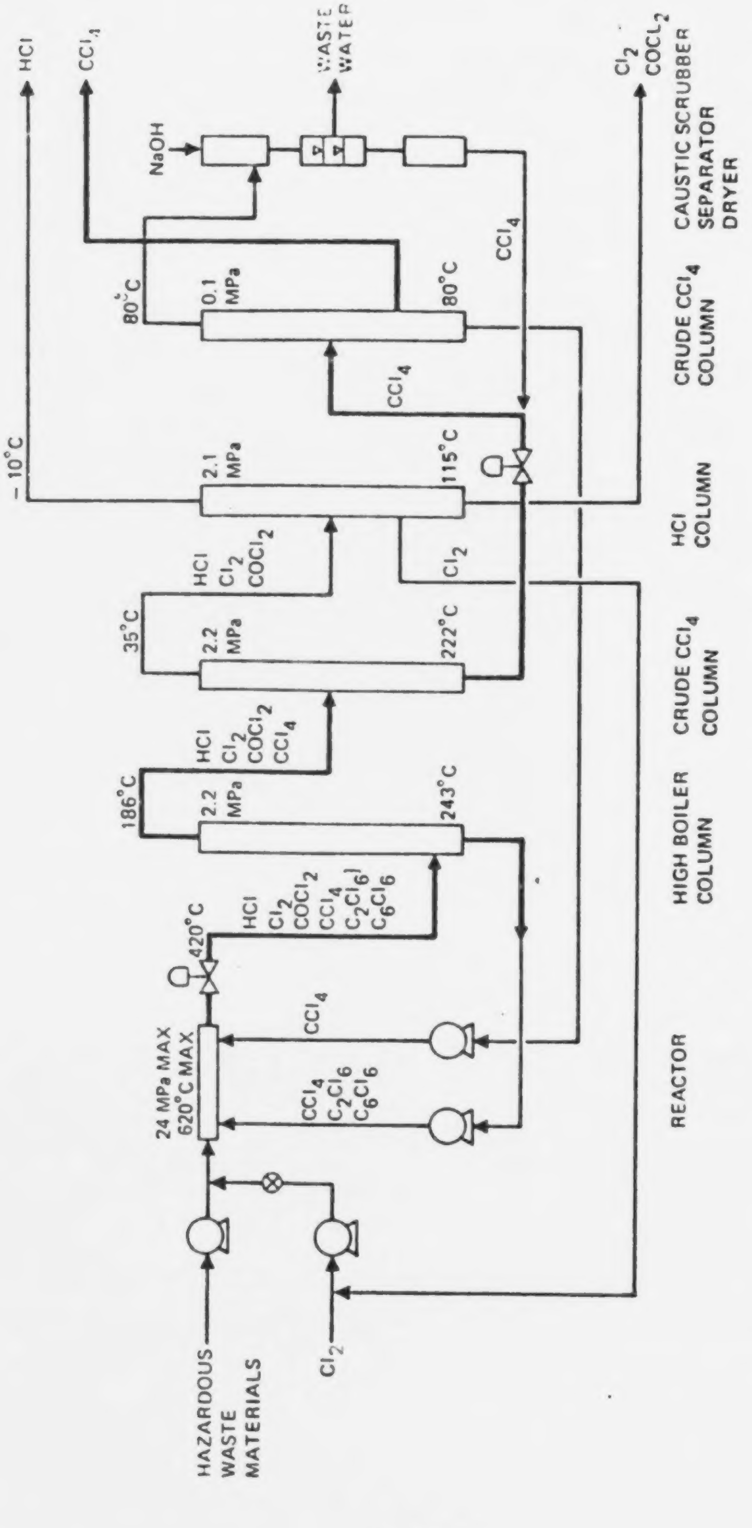

Figure 8.5.1. Schematic diagram of the Hoechst AG chlorolysis process.[5]

8.5.1.1 Pretreatment Requirements--

The feed stream for the Hoechst process should be free of solids to both ensure reaction and to reduce the potential for fouling critical equipment, including pressure control valves and pumps. The particle size of the particulates present in waste hydrocarbon streams (e.g., from ethylene dichloride pyrolysis) are reportedly too fine to remove by conventional filtration. Consequently, an evaporation or distillation method appears more suitable. Fractional distillation is not required.[2]

The feed streams for the Hoechst process may contain up to 5 percent nonchlorinated aromatic hydrocarbons. Higher concentrations make it difficult to limit the design temperature to a maximum of 620°C. Small quantities of oxygen containing organic compounds can also be tolerated, although the phosgene by-product produced by chlorinolysis of such compounds can create serious residual disposal problems.

The presence of elements, other than carbon or hydrogen in a compound, also could result in handling and corrosion problems. Small amounts of sulfur, for example, lead to corrosion of any nickel-containing material. Therefore, sulfur content should be kept below 25 ppm.[2,3]

Nitrogen and phosphorus are also restricted from chlorolysis feedstocks to guard against the possible formation of nitrogen trichloride (NCl_3) and phosphorus trichloride. The first of the compounds is explosive, and the second is pyrophoric.[2,3] The effect of the presence of inorganic contaminants such as metals and water is not clear. According to a representative of the Pittsburg Plate Glass Co., their process is capable of treating metals but will not handle any water or alcohols.[6]

8.5.1.2 Operating Parameters--

As noted in Table 8.4.2, the Hoechst process operates at temperature and pressure conditions that are higher than those used in the three United State's processes. Conditions for operation of the Hoechst process are further shown in Figure 8.5.1 and described in more detail in References 1 through 5. Graphical representations of the amount of chlorine consumption for feedstocks of various Cl:H:C mole ratios are provided in References 1 and 7. As noted in Reference 1, exceed chlorine is used in the Hoechst process in order to operate well outside the explosive range, and to maintain final temperatures at levels below 620°C to avoid corrosion and other problems.

8.5.1.3 Post-treatment Requirements--

The products generated from the Hoechst-Uhde process are carbon tetrachloride, hydrochloric acid, and carbonyl chloride (phosgene) if oxygen is in the feed. The percent yield as a function of feedstock composition is not known. However, it is assumed that the purity of product is sufficient to meet that required for fluorocarbon production since about 80 percent of the carbon tetrachloride produced in the United States is used in the manufacture of Freon-11 and 12 for refrigeration and propellant usage. Thus, disposal would not be a problem except in the case of off-specification product.

The hydrochloric acid produced during the chlorinolysis process could be utilized onsite at a chloro-organic manufacturing facility. For example, the options available include oxyhydrochlorination of ethylene to produce saleable ethylene dichloride or conversion of the acid back to chlorine. Phosgene produced could be sent offsite for use in the manufacture of isocyanates, carbonates and polycarbonates provided chlorine, hydrochloric acid, and carbon tetrachloride are present at acceptably low levels.[2]

The Hoechst process, as shown in Figure 8.5.1, utilizes absorption units to treat waste exit gases. An incineration section (not shown in the figure) equipped with a scrubber is also provided to dispose of pretreatment residues which are not fed to the chlorinolysis unit and all wastewater streams contaminated with traces of chlorinated hydrocarbons. Most trace inorganics, including metals present in the feedstock, will be separated in the pretreatment step, and will be found in the incinerator combustion products.

8.5.2 Demonstrated Performance

The amount of performance data available are minimal, with available performance data previously summarized in Table 8.4.2. The Hoechst-Uhde process appears to be the most viable of the four processes because it is able to process a wide range of wastes, achieves the highest yield of carbon tetrachloride, and creates a minimal amount of undesired residues.

8.5.3 Cost of Treatment

The annual operating cost data shown in Table 8.5.3 are based on data provided in Reference 3 for March 1978. These data have been updated to reflect early 1986 costs. The adjustments were made using the Chemical Engineering Plant Cost Index to estimate capital investment costs and a variety of other sources to determine 1986 material, utility, and labor costs. The 1986 capital investment cost for the chlorolysis plant processing 25,000 metric tons/year of organic chlorine wastes is estimated to be $40,000,000, up from about $27,000,000 in 1978. This cost was based on a site in the Gulf Coast area, with land and startup costs excluded.

Analysis of the cost data as initially provided by Hoechst-Uhde (Reference 8) indicates that the economic feasibility of using chlorolysis as a waste disposal alternative is primarily dependent upon the selling price of carbon tetrachloride and to a lesser extent upon the type of waste available as feedstock. The annual organic costs provided in Table 8.5.3 were based on a mixed waste considered by Hoechst to be the base case since a higher solvent waste (high chloride) content would require preheating of the chlorine reactant and lead to possible corrosion and material problems.

The annual operating cost of $26,552,000 for the base case will be about 25 percent lower than that required for a feedstock consisting entirely of vinyl chloride (VC) monomer waste, due to the difference in chloride requirement. Although this increased costs for the VC waste could be offset by the increased product credits from the sale of carbon tetrachloride (and hydrochloric acid), the return cannot be guaranteed.

The volume of carbon tetrachloride produced by the proposed plant represents about 25 percent of the total market volume, a level which would cause major perturbations in the price structure. The process, however, should be competitive with incineration at existing price levels of about $500/ton of carbon tetrachloride.

TABLE 8.5.3. ANNUAL OPERATING COST FOR PROCESSING 25,000 METRIC TONS/YEAR OF A MIXED VINYL CHLORIDE MONOMER AND SOLVENT WASTE AT A CHLOROLYSIS PLANT

Item	Cost, $/year
Chemicals	
Chlorine: 68,000 metric tons @ $220/metric ton	14,960,000
20% Caustic: 14,500 metric tons @ $70/metric ton	1,015,000
Methane: 134,500,000 ft^3 @ $6/1000 ft^3	807,000
Utilities	
Electric power: 25,600,000 Kw-hr @ $.05/Kw-hr	1,290,000
Steam: 52,000 metric tons @ $13.2/metric ton	690,000
Cooling water: 3.9 x 10^9 gallons @ $0.10/1000 gallons	390,000
Operating Labor	
Operator, 10 men/shift, $12.00/manhour	1,050,000
Direct supervision, 4 men, $15.00/manhour	125,000
Maintenance	
Maintenance labor, 2% of Total Plant Cost	800,000
Maintenance supply, 2% of Total Plant Cost	800,000
Direct Overhead (30% of Operating Labor and Supervision)	350,000
General Plant Overhead (50% of Operating and Maintenance Labor and 3% of Total Plant Cost)	3,175,000
Taxes and Insurance (1.5% of Total Plant Cost)	600,000
Royalty	500,000
Net Annual Operating Cost	26,552,000

SOURCE: Reference 3

8.5.4 Overall Status of Process

8.5.4.1 Availability/Application--

Chlorinolysis is primarily used as a manufacturing process. Its potential as a waste treatment process is seriously limited by its prohibitive capital cost and its dependency on the carbon tetrachloride market. In their feasibility studies of the Hoechst-Uhde chlorinolysis process, both reference 2 and 3 investigators concluded that a regional waste treatment facility would be a possibility. Such a facility would be best located in the Gulf Coast region.[3]

The Hoechst-UHde process is capable of treating C_1 to C_6 organochlorine compounds, including aromatics. Suitable feedstocks include those residues from the production of VCM, chloromethane, propylene oxide, allyl chloride, perchloroethylene, and residues from benzene chlorination.[3]

8.5.4.2 Environmental Impact--

The air emissions and wastewater discharges from a Hoechst-Unde chlorinolysis system processing 25,000 metric tons of waste/year were estimated in Reference 3. The air emissions of volatiles including carbon tetrachloride, phosgene, and chlorine from the plant were less than 1 ton/year and were considered environmentally acceptable. Wastewater emission data were based on concentrations and flows resulting from scrubbing operations. These also were considered to be insignificant from the standpoint of environmental impact.

8.5.4.3 Advantages and Limitations--

Chlorinolysis is not a process that will be used by any waste processing facility, however, it has excellent resource recovery potential. Limitations are the high capital and operating costs and uncertainties regarding the availability of feedstock and the economics of cost recovery through product sales.

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8.6 CHEMICAL DECHLORINATION

Chemical dechlorination methods have been developed as possible alternatives to incineration or land disposal for halogenated organic compounds such as PCBs. Researchers have found that in order to decrease the degree of toxicity, as well as the chemical and biological stability of chlorinated compounds, it is not necessary to totally break down the molecular structure.[1] Instead, the formation of a compound considered harmless and environmentally safe can be achieved through a reaction system that will result in the cleavage of C-Cl bonds or the rearrangement of the chlorinated molecule. Although several different dechlorination methods exist, all of the processes are based primarily on two technologies; the "Goodyear process" developed by Goodyear Tire and Rubber, and the NaPEG system developed by the Franklin Research Institute.

The Goodyear Process was originally developed to reduce PCB laden heat transfer fluids from slightly above 500 ppm to less than 10 ppm. The reaction chemistry is based on the use of a sodium-naphthalene reagent to form sodium chloride and an inert, combustible sludge. The reagent is produced by disolving molten sodium and naphthalene in tetrahydrofuran.[2] However, the reactivity of metallic sodium with water necessitates the use of an air free anhydrous reaction vessel to prevent rapid generation of hydrogen or loss of reagent through the formation of NaOH.

Since Goodyear has decided not to pursue the marketing of this process, several companies such as SunOhio, Acurex, and PPM Inc, have entered the field. Generally, they have modified the process by substituting proprietary reagents for naphthalene, which is a priority pollutant. These processes are also intended for treatment of PCB contaminated oils (50-500 ppm) and require pretreatment to remove water and inorganics such as soil. Typically, these processes cannot handle PCB concentrations greater than 10 percent, and most are not suitable for sludges, soils, sediments, and dredgings. The exception is the Acurex process which uses a relatively nontoxic solvent to extract PCBs from contaminated soils and then destroy them with a proprietary reagent. (see Figure 8.6.1). These treatment methods may have limited applicability for other chlorinated organic compounds; however, more research is needed to determine process feasibility.

A more promising technology is the NaPEG process, originally developed in 1980 by Pytlewski, et al., at the Franklin Research Institute.[3] The intent was to devise a reaction system that would decompose PCBs and representative halogenated pesticides in an exothermic and self-sustaining manner. The dechlorination reagent was formed by reacting alkali metals such as sodium with a polyethylene glycol (M.W. 400) in the presence of heat and oxygen.[4] The reaction mechanism involves a nucleophilic substitution/elimination and the oxidative degradation of chlorine through the generation of numerous free radicals. The process reactivity can be "tuned" or directed at various aliphatic or aromatic systems by varying the molecular weight of the polyethylene glycol.[5] Typical by-products of the reaction are salts such as sodium chloride, hydrogen, and hydroxylated organic derivatives.

Laboratory studies have shown a 99.99 percent reduction of PCBs in dielectric transformer oils and 51.9 percent reduction in PCB contaminated, low moisture soils.[6] In addition to PCBs, the following organohalogens have also been successfully treated by this method; hexachlorocyclohexane, hexachlorobenzene, tri- and tetrachlorobenzenes, pentachlorophenol, DDT, kepone, and chloroethylsulfide. The primary advantages of the NaPEG system (which is generally referred to now as "APEG" - Alkali Polyethylene Glycoates) is that the reagent is not based on a dispersed metallic sodium reaction, can tolerate low levels of water content, and is stable in air. Therefore, the process may by applicable to soils, dredgings, sediments, and low moisture sludges. A summary of the chemical dechlorination methods currently available is presented in Table 8.6.1

Two emerging technologies based on the APEG system are currently under development at the Galson Research and the Sea Marconi Corporations. The

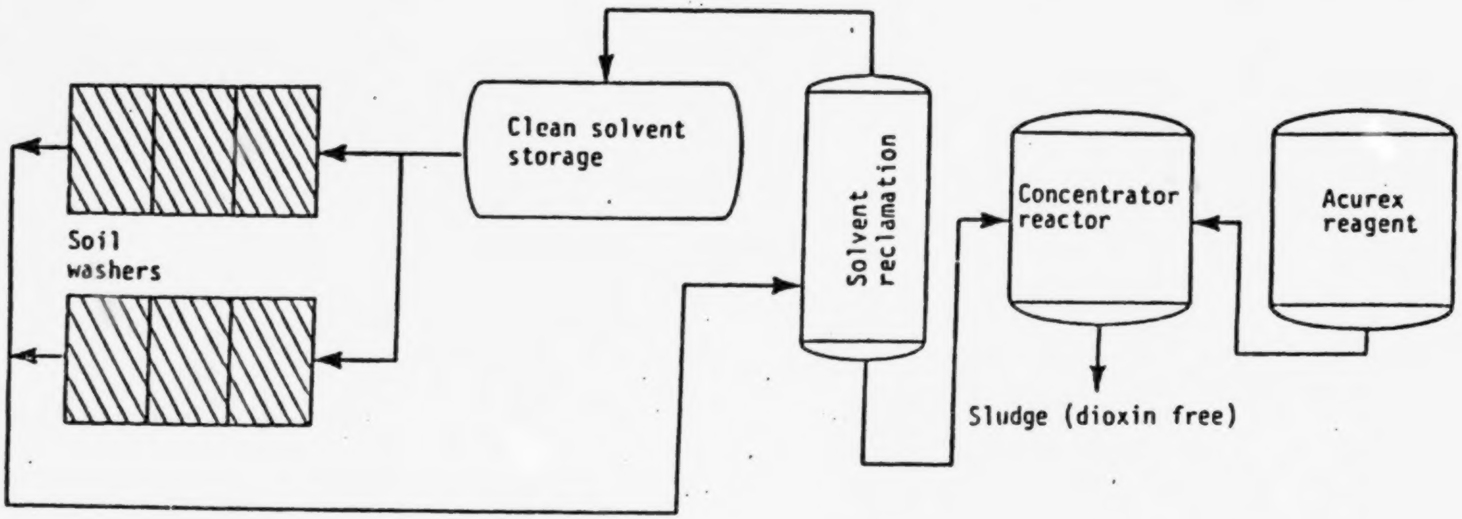

Figure 8.6.1. Soil cleaning process schematic.

Source: Acurex Corporation (Cincinnati, Ohio).

TABLE 8.6.1. DECHLORINATION PROCESSES

Process description	Compounds and forms of waste treated	Destruction Capabilities	Residuals	Comments
PCBs				
• proprietary sodium reagent used to strip away chlorine • oil is mixed with reagent and sent to reactor • mixture is then centrifuged degassed and filtered	• liquid hydrocarbon streams, i.e. PCB contaminated oil from transformers • cannot be used on aqueous or soil wastes	• 250 ppm PCB to 1 ppm • 3000 ppm to below 2 with several passes	• metal chlorides • polyphenyls • treated oil	• mobile, continuous process • moisture and contaminant removal required as pre-treatment • moderate temperature and pressure • pure PCBs destroyed at 150 ml/min
Acurex				
• proprietary sodium reagent used to strip chlorine • contaminated oil is filtered, and mixed with reagent • reaction takes place in processing tank	• can be used on PCB contaminated oils and soils • also effective on transformer oil contaminated with 2,3,7,8-TCDD	• PCB feeds as high as 10% effectively treated • 2,3,7,8-TCDD reduced from 200-400 ppt to 40 ppt	• treated oil • sodium hydroxide effluent • polyphenol sludge	• mobile, batch operation • pretreatment needed to remove water, aldehydes and acids from transformer oils • non-toxic solvent used to extract PCBs from soil
APEG				
• sodium polyethylene glycol reagent (NaPEG) used for PCB • Potassium Polyethylene Glycol **(KPEG) used for TCDD** • reagent is added to contaminated material in the presence of air, and can be sprayed on	• PCB oils and soils • TCDD contaminated soils • also tested on hexachlorocyclohexane, hexachlorobenzene, PCP, DDT, KEPONE, Tri- and Tetrachlorobenzenes	• PCB destruction 99.99% • 2,3,7,8-TCDD reduced from 330 ppb to 101 ppb	• sodium chloride • oxygenated biphenyls • decontaminated material • hydrogen gas	• involves the application of reagent in the presence of air or oxygen • water increases reaction times and decreases the degree of chlorination • temps. above 100°C required fast destruction
PPM				
• proprietary sodium reagent used for chlorine stripping • reagent is addedeto contaminated oil and left to react • solid polymer formed is filtered out	• PCB contaminated oil • TCDD detoxification will be investigated soon • aqueous waste and soil not treated	• 200 ppm PCB reduced to below 1 ppm	• solid polymer • decontaminated oil	• mobile, batch process, 700 gal/hr • polymer is produced at a rate of 55 gal per 10,500 gal oil treated • polymer is regulated and must be landfilled

Source: Reference 6.

Galson Research process involves a series of processes for the degradation of chlorinated benzenes, biphenyls and dioxins from contaminated soils. The system, which was developed under EPA sponsorship, is based on the more reactive KPEG (potassium based) reagent, in conjunction with a sulfoxide catalyst/cosolvent. A probable reaction scheme is presented in Figure 8.6.2. Laboratory results of dioxin testing have shown that destruction efficiencies of 99 percent or greater were obtained using a single soil sample containing 2 ppm of dioxin. Higher destruction efficiencies can be expected for solvents.

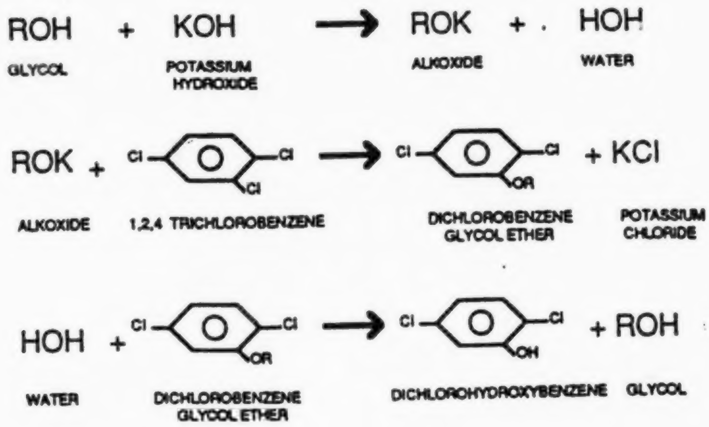

Figure 8.6.2. Probable reaction mechanism.
Source: Galson Research Corporation

The Sea Marconi's chemical process, called CDP-Process, was first developed for the decontamination of PCB-laden mineral oils. However, the system has been more recently applied to materials and surfaces exposed to contaminants coming from fire or explosion of PCB equipment. The chemistry involves reaction with high-molecular weight polyethylene glycol in the presence of a weak base and a peroxide. Hopefully, the continued success of these studies will result in a viable method for the destruction of toxic organo-halogens dispersed as solid waste in the environment. No application to aqueous media can be expected from these processes due to their sensitivity to water.

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4. Ibid pg. 197.

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9.0 BIOLOGICAL METHODS

9.1 PROCESS DESCRIPTION

Biological treatment processes used for the removal of organic solvents and other VOCs from industrial waste streams can be divided into two major categories: 1) aerobic processes, and 2) anaerobic processes. In aerobic systems, microorganisms use oxygen to biologically oxidize compounds. Anaerobic systems do not require oxygen and these anaerobics exist and react in a relatively oxygen free environment. Each of these processes can be further subdivided into suspended growth or attached growth systems. Suspended growth systems are characterized by microbes moving freely within the waste stream or being suspended by mechanical agitation.. Attached growth systems have layers of microbes attached to a suitable medium that comes into surface contact with the waste stream. The following section describes the major biological treatment processes used.

9.1.1 Processes Used for Biotreatment

9.1.1.1 Activated Sludge--

Figure 9.1 presents flow diagrams of representative activated sludge processes. The basic reactor design categories of activated sludge systems include conventional, complete mix, and step aeration. By varying the operating parameters of the systems in Figure 9.1, a system can be defined as a high rate or an extended aeration system. Other modifications are also possible. As noted in Section 7.6, the PACT process, the addition of powdered activated carbon to a biological process, has been used with some success in activated sludge processes to treat solvent wastes. The following paragraphs briefly describe the more conventional activated sludge systems and examples of pure oxygen activated sludge processes.

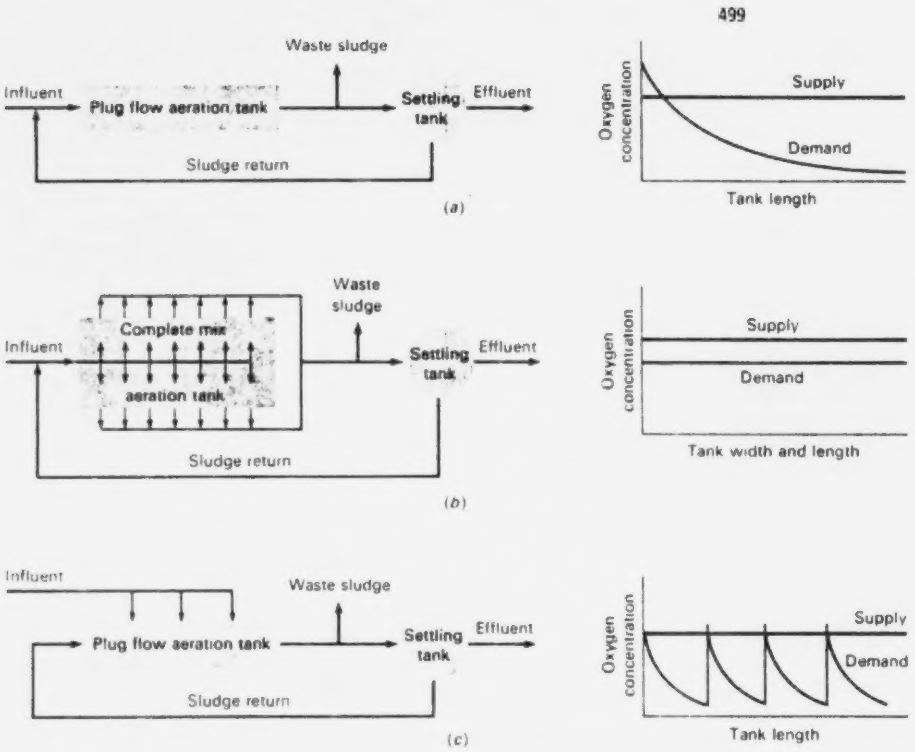

Figure 9.1. Flowsheet and plot of oxygen demand and oxygen supply versus tank length for (a) conventional, (b) complete-mix, and (c) step-aeration activated-sludge processes.

Source: Reference 1.

Conventional Activated Sludge--Figure 9.1a shows a flow diagram of a conventional activated sludge system. Organic waste and recycled sludge are introduced to a reactor where aerobic bacteria are maintained in suspension. The waste stream moves in plug flow through the reactor. A rate of diffused or mechanical aeration supplies the system's oxygen demand and maintains the bacterial suspension. In conventional systems oxygen supply is constant; however, a variation, termed tapered aeration, is designed to provide air in proportion to the reactor's oxygen demand. By aerating more at the reactor entrance where the oxygen demand is greatest, a lower total air requirement is obtained. The waste-sludge mixture remains in the reactor for a mean time known as the hydraulic residence time that is defined as the reactor volume divided by the volumetric flow rate. The sludge mixture flows from the reactor to settling tanks where concentrated sludge is separated from the waste stream. A fraction of the settled sludge is recycled to the reactor and the remainder is wasted. The recycled fraction is determined by the desired food to mass ratio [F/M, measured as biological oxygen demand divided by mixed-liquor suspended solids (kg BOD/kg/MLSS).

Conventional activated sludge processes operate according to a standard set of factors. These factors are: organic loading - measured as F/M ratio; sludge retention time - the average time the sludge remains in the system; hydraulic residence time - the average time the waste sludge remains in the reactor; and the system's oxygen demand.

As noted, variation in design and operation of activated sludge units can be made to accommodate waste stream flows and BOD loadings. For example, extended aeration uses a relatively long hydraulic residence time operated by keeping the F/M ratio relatively low (generally between 0.05 and 0.25 kg BOD/kgMLSS/day). This system provides a high removal efficiency with a minimum of excess sludge. Alternatively, the high rate activated sludge process operates with a shorter aeration period and therefore a higher F/M ratio. High rate systems operate in a more efficient BOD removal range and consequently demonstrate a high rate of BOD removal. The shorter aeration period generates a lower-quality effluent and maximizes wastes sludge.

Complete Mix Aeration--Figure 9.1b represents an attempt to duplicate the hydraulic regime of a mechanically stirred reactor. The influent settled sewage and return sludge flow are introduced at several points in the aeration tank from a central channel. The mixed liquor is aerated as it passes from the central channel to effluent channels at both sides of the aeration tank. The aeration-tank effluent is collected and settled in the activated-sludge settling tank.

The organic load on the aeration tank and the oxygen demand are uniform from one end to the other. As the mixed liquor passes across the tank from inlet ports to the effluent channel, it is completely mixed by diffused or mechanical aeration.[1]

Step Aeration--Figure 9.1c shows the flow diagram of a step aeration system. Step aeration is also an improvement on the conventional activated sludge design. As seen in the flow diagram, the waste feed is introduced at discrete steps in the reactor. This configuration creates a more uniform oxygen demand in the reactor and better utilization of constantly supplied oxygen.

Contact Stabilization--This is a two stage process that provides for reaeration of the return activated sludge in a separate aeration tank. The process was developed to utilize the rapid adsorption of soluble and particulate organic matter by the activated sludge. The adsorptive phase takes place within one hour of aeration in the contact tank. The settled sludge is then aerated to oxidize the organics for an additional 3 to 6 hours in the stabilization tank. Since the sludge is concentrated in the stabilization tank, the total aeration tank volume of the system can approach 50 percent of the volume needed for a conventional system. The contact stabilization process is most successful for waste streams containing nonsoluble organics.

Pure oxygen activated sludge--Pure oxygen activated sludge processes can be designed using any reactor design and aeration system design. These systems are a relatively recent development from conventional aeration systems. Pure oxygen processes are more efficient and can be operated at higher process loading parameters than similarly designed conventional air systems. It is often the case that pure oxygen processes can be run less expensively than air processes in spite of the additional cost of pure oxygen.

Nitrification--The presence of ammonia in wastewater exerts an oxygen demand on the treatment system. In nitrification, ammonia is oxidized biologically to nitrate according to the following processes:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{(Nitrosomanas)}} 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \xrightarrow{\text{(Nitrobacter)}} 2NO_3^-$$

In practice, nitrification can be achieved in the same reactor used for treatment of organic carbon by significantly extending the aeration period, or in a separate suspended growth reactor that follows an activated sludge treatment process. Nitrification is accomplished using either air or pure oxygen.

9.1.1.2 Aerated Ponds and Lagoons--

The aerated pond or lagoon treatment process is analogous to an extended aeration activated sludge process. An earthen basin is used for the reactor. Aeration is performed through surface or diffuse aerators and the biomass is kept in suspension. Historically, aerated lagoons were operated without recycle, however, modern lagoons recycle the biomass. Ponds and lagoons typically rely on algal photosynthesis, adequate mixing, good inlet-outlet design, and a minimum annual air temperature above 5°C to operate effectively. In general, aerated lagoons are used for low to medium organic strength wastes.

9.1.1.3 Aerobic Digestion--

Aerobic digestion is an alternative method of treating the organic sludge produced from various treatment operations. Aerobic digesters may be used to treat 1) waste activated or trickling filter sludge, 2) mixtures of waste activated or trickling filter sludge and primary sludge, or 3) waste sludge from activated sludge treatment plants designed without primary settling. Two variations of the aerobic digestion process are in use: conventional and pure oxygen. Thermophilic aerobic digestion is also emerging as a viable technology.

In conventional aerobic digestion, the sludge is aerated for an extended period of time in an open, unheated tank using air diffusers or surface aeration equipment. The process may be operated in a continuous or batch mode. Pure oxygen aerobic digestion is a modification of this process in which pure oxygen is used instead of air. Thermophilic aerobic digestion represents still another refinement of the aerobic digestion process. Carried out with thermophilic bacteria at temperatures ranging from 25 to 50°C above the ambient temperature, this process can achieve high removals of the biodegradable fraction in very short detention times.

9.1.1.4 Trickling Filters--

A trickling filter consists of a large, highly permeable bed of media onto which microorganisms are attached. The filter media typically consists of stones of 1 to 4 inches in diameter in a cylindical design of 3 to 8 feet tall. The waste liquid is evenly distributed over the top of the filter by a rotary sprinkler. Filters are constructed with an underdrain system that collects the treated liquid and any biological solids that have penetrated the media. The underdrain must be porous to allow air to circulate up through the media. The treated liquid flows to a settling tank where solids are separated from the liquid.

As the waste stream is trickled through the filter media the organics are oxidized by the attached microorganisms. The attached biomass consists of two regions: an aerobic outer layer whose thickness is determined by the depth of oxygen penetration into the biomass, and an anaerobic layer extending from the media surface to the aerobic region. Oxidation of the organics thus occurs through both aerobic and anaerobic processes.

9.1.1.5 Rotating Biological Contactors--

A rotating biological contactor consists of a series of closely spaced circular disks of polystyrene or polyvinyl chloride. The disks are partially submerged in wastewater and rotated slowly through it. Biological growths become attached to the surfaces and eventually form a thin layer over the wetted surface area of the disk. The rotation of the disks contacts the biomass with the organic material in the wastewater and then with the atmosphere for oxygen adsorption.

9.1.1.6 Bioaugmentation--

Bioaugmentation refers to the development and use of specialized organisms known as chemostatic organisms or chemostats to decompose specific waste streams. Chemostats are cultured to degrade specific wastes and have the potential to capitalize on specific characteristics of industrial wastewater such as its high strength, well-defined composition relative to domestic wastewater, often unusual pH, temperature, and mineral content. Examples of chemostats include the aerobic fungi Aureobasidium pollutants.sp. NO. 14 (FRI 4197 and FERM BP-1) isolated by Kaneko, et al., that lends itself to contact oxidation processes and decomposes and removes solvents such as benzene, xylene, toluene, and autoldehyde, and seven strains of Pseudomons cepacia var., niagarous (ATC 31939-31945) isolated by Caloruotolo, et al, that have been found to degrade some chlorinated aromatics to CO_2, salt, and H_2O.[2] Bioaugmentation can be used to supplement any of the treatment processes described.

9.1.1.7 Anaerobic Digestion--

Anaerobic digestion is one of the oldest processes used for sludge stabilization. It involves the oxidation of organic and inorganic matter with anaerobic and facultative organisms in the absence of molecular oxygen and is carried out in an air-tight container. Anaerobic digestion is actually a two-step process in which acid forming bacteria convert complex organics to volatile organic acids followed by methane producing bacteria converting the volatile organic acids to methane and carbon dioxide. The methane producing process is the reaction rate limiting step and is highly sensitive to acidic conditions. Production of methane will gradually decrease as acidity increases and will cease if the pH drops below 6.5. For this reason the pH of the digester must be monitored and lime may be added as needed. In a stable reactor, gas is produced at a rate of about 1 liter per gram of volatile acids consumed. The final gas produced is generally more than 50 percent methane with between 30 and 35 percent CO_2. The remaining gas consists of other gases such as elemental nitrogen.

The anaerobic bacteria are highly thermophilic and operating temperatures are generally in the range of 85-90°F. The methane gas is often recovered and used to keep the reactor operating in this temperature range.

Anaerobic reactors are highly sensitive to toxic loads, especially to high concentrations of ammonia, heavy metals, and sulfide. If SO_4 is present it will be reduced to H_2S which is often a cause of odor problems in the produced gas.

9.1.2 Operating Parameters

A number of operating parameters cooperatively determine the effectiveness of biological treatment processes. The most influential operating factors are:

- Organic loading described by the food to biomass ratio (F/M often measured in units of kg BOD/kgMLSS · day).
- Sludge retention time or sludge age.
- Hydraulic residence time.
- Fraction of sludge recycled described by the recycle ratio.
- Numerous factors for anaerobic systems such as pH, temperature, toxic loadings, and biocarbonate alkalinity.

Table 9.1 lists general ranges of operating parameters for many of the biological processes discussed in the previous section.

9.2 DEMONSTRATED PERFORMANCE

A literature search revealed a tremendous volume of performance data for biological treatment systems. Unfortunately, the field data are consistently reported as BOD or COD reduction and only infrequently reported as specific organic compound reduction. Pertinent organic compound data have been found for aerobic treatments using activated sludge. aerated lagoons, and in-situ

TABLE 9.1. TYPICAL OPERATING PARAMETERS FOR BIOLOGICAL TREATMENT PROCESSES[3]

Process		Organic Loading (F/M)		Sludge Age, θ_c (days)	Residence Time, θ (hr)	Recycle Ratio, R	Produced (ft^3/1b MLVSS)
		$\frac{\text{kg BOD}_5}{\text{kg MLVSS-day}}$	$\frac{\text{1b BOD}_5}{\text{ft}^3\text{-day}}$				
Conventional and CSTR		0.2-0.6 (0.30)	0.020-0.040 (0.035)	3-14 (5)	4-8 (7)	0.15-0.75 (0.30)	
Step aeration		0.2-0.5 (0.30)	0.040-0.060 (0.050)	3-14 (5)	4-8 (5)	0.2-0.8 (0.30)	
Contact stabilization	Contact tank	0.2-0.5 (0.35)	0.07⁺	3-14 (5)	0.5-1.5 (1.0)	0.2-1.0 (0.40)	
	Stabilization tank				3-6 (5)		
High-rate		0.4-1.5	0.075-0.10	0.25-3	1-3	1.0-5.0	
Extended aeration		0.05-0.25	<0.025	>10	15-30	0.7-1.5	
Pure oxygen		0.4-1.0	0.15-0.25		1-3	0.25-0.5	
Nitrification		10^{-3}-10^{-2} NH_3-N (3 x 10^{-3})		5-25 (10)		0.5	
Anaerobic digestion	Conventional		0.04-0.1 (1b MLVSS/ ft^3·day		720-1440		
	High Rate		0.15-0.40 (1b MLVSS/ ft^3·day		240-720		0.6-0.7

⁺Based on combined volume of contact and stabilization tanks.

( ) typical operating value.

Source: Reference 3.

bioaugmentation. Their removals are reported along with waste characteristics, treatment process type, and other pertinent data in Table 9.2. The literature search revealed no solvent/low molecular weight organic removal data for any anaerobic systems.

The table demonstrates that many priority solvents, some other solvents, and a few ignitable organic compounds reported to have been successfully degraded using aerobic biological treatment processes. Activated sludge is the most commonly reported process and is the most widely available. Aerated lagoons are reported considerably less than activated sludge, as is the use of bioaugmentation. The data indicate that high removal efficiencies may be obtained using properly designed aerobic biological treatment systems.

EPA, in its background document for solvents, has provided performance data, as shown in Table 9.3. Research articles demonstrating the biodegradability (60 to 99+ percent removal) of acetone, n-butyl alcohol, cresols, ethyl acetate, pyridine, and 1,1,1-trichloroethane are also identified in Reference 7. The biodegradability of other solvents of concern is expected to be similar.

9.3 COST OF TREATMENT

Widespread use of aerobic biological treatment systems has led to standardization of their capital and annual operational, materials, and labor costs based upon system capacity. Expected treatment system outlays can be determined using Table 9.4 and Figures 9.2 and 9.3. Since the cost data are in 1971 dollars, updating can be performed using the periodically published indexed such as the EPA Index, the Engineering News Record Index, and the Chemical Engineering Index. 1986 costs are roughly 2.5 times those estimated for 1971. Table 9.4 and Figure 9.2 and 9.3 do not include the additional costs of seed chemostatic organisms to be used in bioaugmented processes. More complete and up-to-date cost information can be found in EPA's Estimating Water Treatment Costs.[9] However, the breadth of this document prevents its inclusion in this section. The data, as presented in Table 9.4 and Figures 9.2 and 9.3, do show the relative costs and scaling factors used for various cost elements.

TABLE 9.2. REMOVAL DATA FOR BIOLOGICAL PROCESSES

Chemical name	Problem concentrations[8]		Influent characteristics	Percent removal range (median)	Removal process
	Substrate limiting (mg/L)	Nonsubstrate limiting (mg/L)			
Priority Solvents					
1,1,1-trichloroethane				99- 99	1
					3
					4
1,1,2-trichloro-1,2,2-trifluoroethane			82 ppb	99.9	
1,2-dichlorobenzene				69- 99	1
					3
1-butanol	--	1,000	42 lb BOD/day per/1,000 ft^3	95-100	1
				98	2
				70-90	3
acetone	--	1,000	100-600 ppb	50	1
			70-90		3
carbon disulfide				(98)	1
carbon tetrachloride			0.117 ppm	100	
			6.5 ppb	99.9	
chlorobenzene				38- 99	1
				(99)	4
			9.05 ppm	99.6	5
			200 ppm	100	

(continued)

TABLE 9.2 (continued)

Chemical name	Problem concentrations[8]		Influent characteristics	Percent removal range (median)	Removal process
	Substrate limiting (mg/L)	Nonsubstrate limiting (mg/L)			
cresols				(99)	1
				95-96	1
ethyl acetate	1,000	--	167 mg/L	99.7	
ethyl benzene	1,000	--		95-100	1
				95-100	2
				90-100	3
			154 ppm	99.8	4
iso-butyl alcohol (sec-butanol)	--	1,000		98.5	1
methanol			42 lb BOD/day per 1,000 ft^3	75-85	1
				84	2
				30-50	3
methyl ethyl ketone			257 mg/L	99.6	4
methyl isobutyl ketone	1,000	100-300			
methylene chloride				69-99	1
				91-97	
nitrobenzene				98	1

(continued)

TABLE 9.2 (continued)

Chemical name	Problem concentrations[8]		Influent characteristics	Percent removal range (median)	Removal process
	Substrate limiting (mg/L)	Nonsubstrate limiting (mg/L)			
tetrachloroethylene				55- 99	1
				(99)	3
toluene				17- 99	1
				95- 99	3
			31 ppm	98.3	4
			17 g/L	99.9	
trichloroethene			214 ppb	99	1
(1,1,1-trichloroethylene			78 ppb	100	
trichlorofluoromethance				(96)	1
xylene			20-200 ppb	93-95	1
			1,250 ppm	99.8	5
1,1,2-trichloroethane				(99)	1
			1.3 ppm	99.7	6
1,2-dichloropropane				99	1
aniline				94.5	1
			500 ppm	100	
benzene				75- 99	1,2
				90-100	3

(continued)

TABLE 9.2 (continued)

Chemical name	Problem concentrations[8] Substrate limiting (mg/L)	Nonsubstrate limiting (mg/L)	Influent characteristics	Percent removal range (median)	Removal process
bis(chloromethyl)ether				(99)	1
bromoform			0.4-1.9 ppb	100	1
chloroform				9- 99 (99)	1
ethylene dichloride (1,2-dichloroethane)	150-500	--	258 ppm	98.5	
ethylidene dichloride (1,1-dichloroethane)			580 ppb	32.9	
O-dichlorobenzene			200 ppm	100	
Ignitable Componds					
acrolein			62 ppm	99.9	1
acrylic acid				85-95 50-70	1 3
allyl alcohol	--	1,000			
dimethylamine	--	300-1,000			

(continued)

TABLE 9.2 (continued)

Chemical name	Problem concentrations[8]		Influent characteristics	Percent removal range (median)	Removal process
	Substrate limiting (mg/L)	Nonsubstrate limiting (mg/L)			
ethanol (acetaldehyde)			42 lb BOD/day per/1,000 ft^3	85-95	1
ethyl acrylate	600-1,000	300-600	42 lb BOD/day per 1,000 ft^3	95-100 95-100	
				95-100 95-100	2 3
ethylene diamine				97.5	1
formaldehyde	--	50-100	3,000 ppm	99	
paraldehyde				30-50	3

NOTES:

Removal Process

1 activated sludge
2 completely mixed activated sludge
3 aerated lagoon
4 bioaugmentation
5 biodegradation using mutant pseudomonas
6 activated sludge with powdered activated carbon

Source: References 4, 5, 6, 7, and 8.

TABLE 9.3. AVERAGE PERFORMANCE OF FULL-SCALE BIOLOGICAL TREATMENT FACILITIES FOR SOLVENTS OF CONCERN (mg/L)

Compound	Type of treatments	Average influent concentration (range)	Average effluent Concentration (range)
Carbon tetrachloride	AS	6.00 (0.192-44.0)	0.010 (NA)
Chlorobenzene	AS, AL	9.88 (3.04-49.8)	0.292 (0.017-1.33)
1,2-Dichlorobenzene	AS, AL	5.70 (2.08-23.3)	0.302 (0.010-1.15)
Ethylbenzene	AS, AL	8.45 (2.21-80.0)	0.010 (NA)
Methylene chloride	AS	2.30 (1.64-3.91)	0.011 (0.010-0.026)
Nitrobenzene	AS	0.765 (0.140-2.32)	0.010 (NA)
Tetrachloroethylene	AS, AL	0.435 (0.036-2.25)	0.010 (0.010-0.019)
Toluene	AS, AL, TF	20.9 (2.08-160)	0.066 (0.010-1.45)
Trichloroethylene	AS	0.231 (0.134-0.484)	0.011 (0.010-0.016)

AS = Activated Sludge
AL = Aerated Lagoon
TF = Trickling Filter
NA = Not Applicable

Source: Reference 7; derived from Office of Solid Waste Analysis of Organic Chemicals, Plastics, and Synthetic Fibers Industries Data Base.

TABLE 9.4. ESTIMATED CAPITAL COST FOR WASTEWATER TREATMENT UNITS[3]

Treatment Unit	Parameter	Model Cost* (1971 dollars)
Raw wastewater pumping	Capacity (mgd)	$C = 2.6 \times 10^3 (mgd)^{1.0}$
Screening, grit removal and flow measurement	Capacity (mgd)	$C = 27.0 \times 10^4 (mgd)^{0.62}$
Equalization	Volume (mg)	$C = 7.2 \times 10^4 (mg)^{0.52}$
Primary sedimentation or secondary clarification	Surface area (in 1000 ft^2)	$C = 2.8 \times 10^4 (A)^{0.88}$
Aeration-basin	Volume (in 1000 ft^3)	$C = 4.2 \times 10^3 (V)^{0.79}$
Aeration-diffused air system	Blower capacity (in 1000 cfm)	$C = 9.0 \times 10^4 (cap)^{0.72}$
Aeration-surface	Capacity (horsepower)	$C = 1.0 \times 10^3 (hp)^{0.89}$
Trickling filter	Media volume (in 1000 ft^3)	$C = 3.4 \times 10^3 (V)^{0.84}$
Recirculation pumping	Capacity (mgd)	$C = 2.0 \times 10^4 (mgd)^{0.70}$
Sludge digesters and buildings	Sludge volume (in 1000 ft^3)	$C = 1.4 \times 10^4 (V)^{0.64}$
Lagoon	Volume (mg)	$C = 7.2 \times 10^4 (V)^{0.71}$
Vacuum filtration	Filter area (ft^2)	$C = 5.9 \times 10^3 (A)^{0.67}$
Centrifugation	Capacity (gpm)	$C = 3.3 \times 10^4 (gpm)^{0.54}$
Incineration	Dry solids capacity (lb/hr)	$C = 1.4 \times 10^4 (cap)^{0.56}$

*1986 cost indicies - 2.5 times 1971 values.

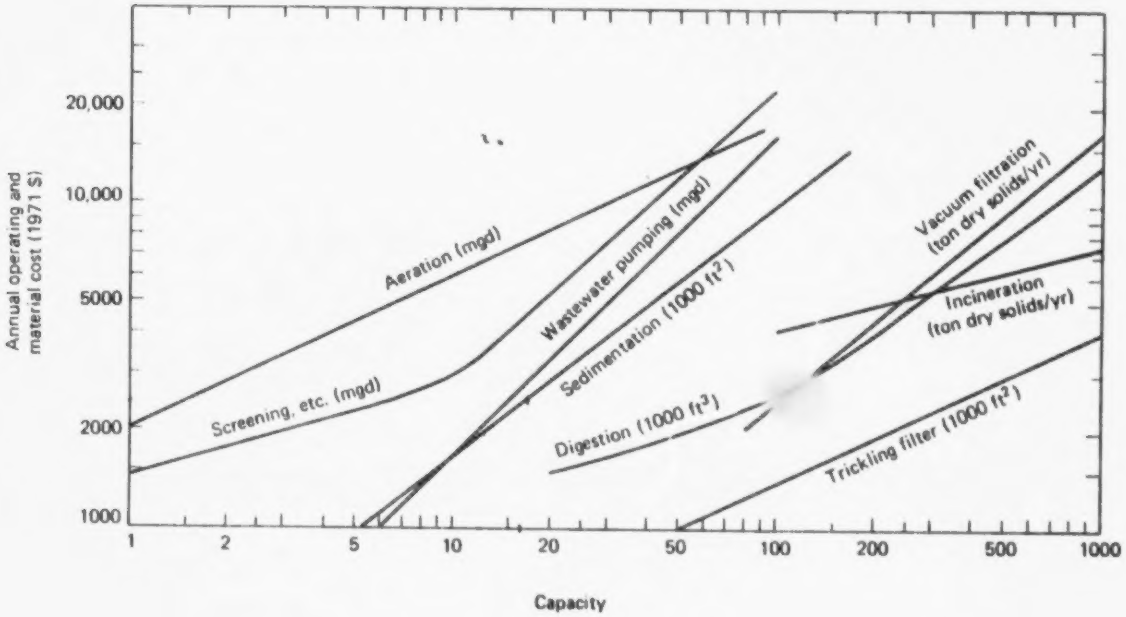

Figure 9.2. Estimated annual operating and materials costs as a function of wastewater treatment facility capacity(3) 1986 costs are ~2.5 times those shown.

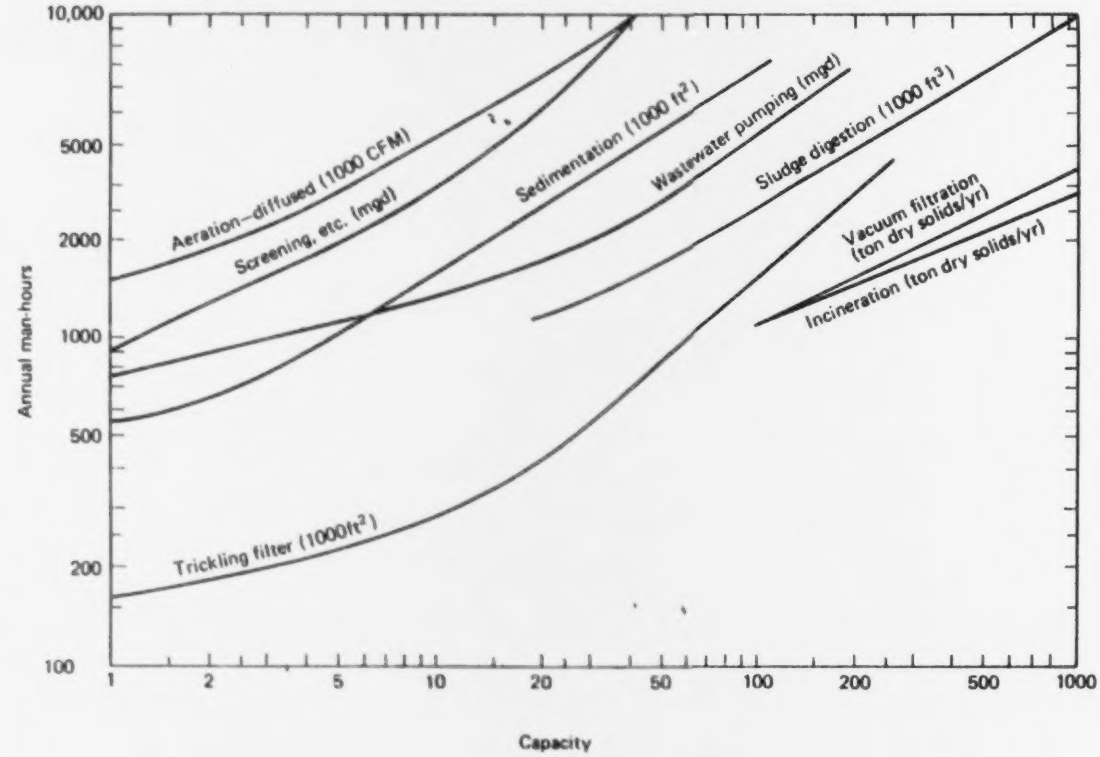

Figure 9.3 Estimated annual man-hours needed for wastewater treatment facility operation.(3)

Standardized cost data for anaerobic treatment systems were not found. An example of a modern anaerobic system is the "Celrobic" process developed by Celanese.[3] In 1983, a 1.08 million gallon/day influent COD of 3.3g/L, Celrobic plant in Pampa, TX, incurred outlays of $8.1 million in capital and $400,000 in expected annual operating costs (1982 dollars). This plant was expected to produce 220 million cubic feet of methane gas annually which helped reduce its expected operating costs considerably.

Actual treatment costs for organic compound removal from a particular waste stream will depend upon specific characteristics of the treatment system design and waste stream. Pertinent data needed for cost estimation are: waste stream volumetric rate, organic compound constituents and concentrations, other waste characteristics such as influent BOD, COD, or level of toxins, treatment design, and overall treatment goal.

9.4 OVERALL STATUS OF BIOLOGICAL TREATMENT

A large number of companies exist that specialize in the design and construction of biological treatment systems. Aerobic systems are the most readily available, and their design and operation are complex but manageable. The total number of biological treatment systems used for organic compound removal is unknown. However, the total number of facilities using some sort of aerobic biological treatment for biodegradable wastes is large, in excess of 2000.[7] The number of companies offering expertise in bioaugmentation and anaerobic treatment is relatively small, but this segment is expected to grow rapidly.

Biological treatment of solvents/ignitables is capable of high removal efficiency and is generally used as the only treatment system or as the final stage in a series of treatments. A treatment train including wet air oxidation units, air stripping treatments, or carbon filters may be used to remove concentrated solvents prior to degradation. No data were found that describe typical applications of biological treatments for organic solvent removal, although most organic solvents of concern can be found in all municipal waste treatment systems.

Aerated treatment systems are generally open surface impoundments and require large land areas and considerable capital investments. Aerated processes have the potential to produce significant air (and odiferous) emissions. Being open to the environment, the treatment plants are subject to weathering and their design features and biological kinetics are stressed by precipitation and temperature extremes.

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10.0 INCINERATION PROCESSES

10.1 OVERVIEW

Incineration is the principal disposal alternative to land disposal for nonrecoverable, flammable solvent hazardous wastes. Incineration possesses several advantages as a hazardous waste disposal technology for solvent hazardous wastes, including the following:

- Thermal destruction by incineration provides the ultimate disposal of hazardous wastes, minimizing future liability from land disposal;
- Toxic components of hazardous wastes can be converted to harmless or less harmful compounds;
- The volume of waste material may be reduced significantly by incineration; and
- Resource recovery (i.e., heat value recovery) is possible through combustion.

Incineration processes range widely in overall complexity, but essentially involve a basic oxidation/pyrolysis reaction (for this discussion, pyrolysis reactors will be considered as a class of incineration processes). Solvent hazardous wastes are largely, if not completely, comprised of organic compounds, thus, the basic incineration process involves the following oxidation equation:

$$C_xH_yCl_z + O_2 \quad CO_2 + H_2O + HCl$$
$$+ \text{ others (including lower hydrocarbons, } Cl_2 \text{ gas, CO)}$$

In this reaction, heat energy first volatlizes the organic constituent, then begins to disrupt the intramolecular bonds, causing the molecules to break down (pyrolyze). Oxygen then contacts the organic components and there reaction ensues. The completeness of the reaction depends upon the combustion temperature, the reaction time, and the availability of oxygen.

Numerous incineration processes are currently commercially available which have been demonstrated to be highly effective for the destruction of solvent hazardous wastes. According to a recent survey(1) more than 5.5 million tons of hazardous wastes were thermally destroyed in 1981, with 1.7 million tons burned in 240 incineration facilities. An increase in incineration use and capacity can be expected because of the land disposal bans. The incineration technologies which have found the most widespread usage are generally those which employ a simple enough process to be applicable to many different types of wastes. Five technologies in particular comprise the vast majority of the currently operating incineration capacity for which data have been developed demonstrating their applicability to the destruction of solvent and other low molecular weight, organic bearing wastes. These are:

- Liquid injection incinerators;
- Rotary kilns;
- Fixed hearth incinerators;
- Multiple hearth incinerators; and
- Fluidized-bed incinerators.

Liquid injection, fixed hearth, and rotary kiln incinerations are most common.(2) The comparatively new starved-air fixed hearth units are generally more efficient than standard designs and are often used for solid hazardous waste disposal. However, this discussion will emphasize liquid injection and rotary kiln units because of their documented ability to destroy wastes. Other thermal treatment technologies, including use as a fuel and several innovative thermal technologies, will be discussed in following sections. Technologies such as wet air oxidation and supercritical oxidation which could be classified as basically thermal in nature, have already been discussed in Section 8, Chemical Treatment Processes.

The key element in selecting incineration in general, as a technological option for waste management, and any incineration design in particular, is the physical and chemical characteristics of the wastes. As discussed previously, solvent hazardous wastes have widely varying characteristics, Most commercial incinerators restrict the types of wastes they will accept based on their applicability to their particular incineration system. Waste characteristics dictate pretreatment requirements. materials transport procedures, and post-treatment techniques. In general, however, at least one incineration method is applicable to all solvent hazardous wastes, unless one or more of the following conditions hold such that incineration and its associated pretreatment/post-treatment are not technologically or economically viable:

a. The waste cannot be physically introduced into an incinerator, even after pretreatment.

b. Constituents are present in the waste which would destroy the incinerator or result in its rapid deterioration.

c. No site and/or disposal method is practicably available for the environmentally sound disposal of ashes and other residues.

d. For wastes having a heat content too low to sustain combustion, no supplementary fuel is available.

e. Agency or Congressionally mandated "acceptable risk" levels are too low to be met by incineration systems.[3]

While incineration as a hazardous waste management technique possesses many potential advantages, there are also two major potential drawbacks: environmental impacts, and costs. Incineration has the potential to affect both air and surface waters via stack emissions and fugitive emissions of volatile compounds, and the production of solid wastes (ash and scrubber liquors and scrubber sludges).

Incineration facilities permitted to operate by EPA under RCRA are required to achieve at least a three tiered environmental standard:(4)

1. They must achieve a destruction and removal efficiency (DRE) of 99.99 percent for each principal organic hazardous constituent (POHC);
2. They must achieve a 99 percent HCl scrubbing efficiency or emit less than 4 lbs/hr of hydrogen chloride; and
3. They must not emit particulate matter in excess of 0.08 grains/dscf, (0.18 grams/dscm) corrected to 7 percent oxygen.

Other standards which may affect the decision to incinerate solvent hazardous wastes include limitations on the generation of CO, SO_x, NO_x, and toxic air pollutants (e.g., toxic metals) air standards. To become permitted, an incineration facility must submit to a full scale evaluation of design and performance. This evaluation includes a trial burn monitored by EPA, demonstrating the ability to perform to expected levels for various wastes. Most incinerators are equipped with control systems to limit both particulate matter generation and acid gas emissions. Since solvent hazardous wastes commonly contain chlorine, the latter is needed to remove HCl, a major product of chlorinated organic compound incineration.

Costs of incineration are higher than most hazardous waste management alternatives. Incineration costs more because of the large energy input requirements and cost of environmental controls. Costs vary widely depending upon waste characteristics, incinerator design, and various operational considerations. Costs of commercial incineration were found to vary from approximately \$0.10/lb to \$3.00/lb.[5] The costs associated with constructing an incineration facility at a generation site are very large. Typically they range from several hundred thousand to several million dollars. Incineration may, however, provide a cost benefit in comparison to other disposal alternatives. Incineration may be used to provide usable heat energy both for process and space heating purposes.

10.1.1 Chemical Processes Involved in Incineration

The chemical reaction sequence which takes place in the destruction of hazardous wastes in an incinerator is a complicated process. It involves a multiple series of decomposition, polymerization, and free radical reactions. Several intermediate stages may occur before the original matter is completely oxidized into its final product, depending upon the chemical composition of the waste and the design and operation of the incinerator. The chemical process may be considered as consisting of three basic steps, as detailed below.

1. Application of Heat Energy--

Most incinerators operate in a flame mode (i.e., wastes pass through a superhigh temperature zone, followed by a combustion zone at high heat). Heat energy acts upon the constituents of the waste in two ways. First, heat energy raises the energy level of individual molecules, leading to waste particle dispersion (e.g., volatilization). Second, heat energy pyrolyzes molecules, breaking down intramolecular bonds, allowing reactive species to form.

2. Mixing with Combustion Air/Reactants--

Oxygen is applied to the reactor and is brought into contact with the reactive species of the waste. The effectiveness of the reactor in bringing oxygen into contact with the reactants is the key element in the overall effectiveness of the unit. The dispersion of waste species, e.g., by atomization, and the turbulence applied by combustion system mechanisms, is thus a key element increasing the destruction effectiveness of the system. Gaseous wastes, burn more readily than liquids, dispersed liquid droplets more readily than liquids in bulk, and liquids more readily than bulk solids.

3. Formation and Separation of Combustion Products--

As oxidation reaction ensues, gaseous and solid byproducts form and begin to separate. Some solid byproducts and noncombustable solid waste constituents fall into the bottom of the combustion unit, while gaseous (and vaporous) byproducts are exhausted out of the unit toward air pollution control and heat recovery. However, most incinerators in 1981 were not equipped with air pollution control devices, probably because these facilties handled only low ash, nonhalogenated liquid wastes for which control measures are not usually necessary.(6)

The typical chemical reaction scheme for incineration of hazardous wastes is shown below:

$C_xH_yCl_z + M$ + nO_2

waste mixture including noncombustable solid (M) + stoichiometric volume of oxygen

$\longrightarrow CO_2 + H_2O + HCl + M$

most common reaction products

$+ [Cl_2 + C_aH_bCl_c + \text{others}]$

and other species including incompletely combusted species, noncombustible species

In practical operations, the incinerator is operated to minimize as much as possible the formation of the second group of products listed above.[7] The formation of organics as byproducts is considered a consequence both of inefficient operation and of the contribution of organics from fuels and reformation. The formation of Cl_2 gas, which is highly toxic, is very undesirable because it is relatively difficult to remove from stack gases by conventional air pollution control systems. Fortunately, almost all chlorine is emitted as HCl, but auxiliary fuel is often utilized as much for its contribution of sufficient hydrogen to suppress Cl_2 formation as for its contribution to the overall heat value of the combustion mixture.[7]

Although the reaction scheme in incineration is highly complex, the overall high rate of reaction allows the general reaction scheme to be described in terms of first order kinetics. The kinetics if the reaction serve to indicate the importance of several operational factors as shown below:

$$\frac{-dC_A}{dt} = k\,(C_A)$$

where C_A = concentration of constituent A in the waste
k = reaction rate coefficient
t = time

The reaction rate coefficient is a function of waste and operating characteristics, as indicated below:

$$k = Ae^{-E/RT}$$

where A = Arrhenius coefficient (characteristic parameter)
E = activation energy (characteristic parameter)
R = universal gas constant
T = absolute temperature[8]

Thus, the most significant factors impacting the destruction of wastes in an incinerator include the temperature, time, turbulence, and concentration of principal constituents. This observation has been supported by practical experience, although these is no absolute level of these factors that could be correlated with DRE or PIC formation.(6)

10.1.2 Applicability of Incineration to Solvent Hazardous Wastes

The determination of the applicability of incineration in general, and specific incineration technologies in particular, to the management of hazardous wastes is based upon the analysis of waste physical and chemical characteristics. The overall "incinerability" of specific wastes is a function of the relative ease with which those materials may be input to the combustion system, the ignitability and combustibility of the materials during the oxidation/pyrolysis process, the relative hazardousness of potential combustion byproducts (dictating post-combustion handling and control), and the general impact on the system from their incineration. Several chemical and physical characteristics of the wastes, must be considered in determining whether incineration is technically and/or economically feasible, what incinerator design will handle a waste most effectively, and what form of pretreatment should be performed to enhance effective performance. By virtue of their characteristics, solvent hazardous wastes, in general, are considered highly applicable to incineration.

"Hazardous wastes to be burned in an incinerator, including solvent hazardous wastes, may be classified into two basic categories relative to their incinerability as follows:

1. Combustible wastes--which sustain combustion without the use of auxiliary fuels; and
2. Noncombustible wastes--which will not sustain combustion without the use of auxiliary fuels."[9]

All combustible wastes are obviously applicable to incineration, but this may not be the best disposal option for such substances. As discussed in the next section, such wastes may be better handled in fuel burning devices such as industrial boilers specially designed to burn hazardous wastes, which would make more effective use of the recoverable heat energy from these substances. The primary focus of this discussion will be on noncombustible wastes. Noncombustible wastes exhibit characteristics which limit their combustibility. Whether or not these limitations will present a technological or economic barrier to incineration must be determined.

The primary waste characteristics examined to determine the relative "incinerability" include the following:

- Physical form;
- Heat content/heat of combustion;
- Autoignition temperature/thermal stability;
- Moisture content;

- Solids content/metals content/inorganic content;
- chlorine content;
- viscosity; and
- corrosivity.

These characteristics impact all phases of the incineration process. A brief discussion of the impact of each of these characteristics is presented below.

Physical Form--

The gross physical form of a waste is the primary consideration in the selection of an appropriate technology, including input of feed mechanism. Solids, liquids, gases, slurries, and sludges all perform very differently in an incinerator. Physical form may be modified by some pretreatment or may change under the high heat conditions of the combustion chamber. Physical form may especially impact the residence time within an incinerator. A liquid waste may not, for example, be retained long enough in a rotary kiln to allow for effective combustion. Sludges may not disperse well and may clog a fluidized-bed. Physical form has some impact on costs of incineration, particularly in the handling and transport of wastes to the incinerator. In general, solid wastes are easier to handle and are, therefore, less costly to deal with than liquid wastes.(9)

Most solvent hazardous wastes occur as either liquid or slurry. A relatively small percentage of the volume of solvent hazardous wastes are present as solids containing spent solvent. The impact of different physical forms of solvent hazardous wastes on applicability to different incineration and thermal destruction technologies is not considered significant for some technologies including rotary kilns, multiple hearth, pyrolysis, and fluidized-beds, but is significant for others such as liquid injection and fixed hearth incinerators.[10]

Heat Content/Heat of Combustion--

The heat of combustion (or heat content) of a substance is defined here as a measure of the amount of heat energy produced when the substance is combusted. Wastes with a higher heat content will produce a higher flame temperature when burned, which will in turn produce higher destruction efficiencies.

The heat content of wastes has been the most commonly used characteristic for ranking their incinerability, Heat of combustion is often used as a guideline for determining the need for employing auxiliary fuel. Wastes with a heat content above 8,500 Btu/lb are considered fuels, and can be burned in facilities regulated under RCRA Subpart D. These wastes can sustain combustion in most furnaces. Between approximately 2,500 and 8,500 Btu/lb wastes may require auxiliary fuels to sustain combustion. Below 2,500 Btu/lb, wastes require auxiliary fuels and, in many cases, other forms of pretreatment before incineration.[3] A good example of such wastes are those with high moisture contents, which sometimes require dewatering before incineration can be conducted. High moisture and chloride contents both limit incinerability (as discussed later in this section). Heat of combustion for solvent wastes are listed in Table 10.1.

Autoignition Temperature/Temperature Indicators--

Autoignition Temperature (AIT), as well as several other temperature based experimental parameters, have been used as indicators of relative incinerability. AIT is defined as the temperature at which a waste will first sustain combustion. In theory therefore, the lower the AIT of a material, the lower the required combustion temperature, and thus, the more easily it will be to incinerate. AIT is considered somewhat limited as an indicator parameter because it does not take into account other waste characteristics which may limit incinerability in specific systems.[11(e)]

Two other temperature based parameters described in the literature which have been developed as incinerability indicators are the practical lower limit for incineration (T_{LL}), and the temperature required for 99.99 percent destruction (T_{99}). T_{LL} was estimated from test burn data for a variety of

TABLE 10.1. SOLVENT HAZARDOUS WASTE HEATS OF COMBUSTION

Compound	Heat of Combustion (Btu/lb)	Compound	Heat of Combustion (Btu/lb)
Trichloromonofluoromethane	198.5	Propylene Glycol	10,196.6
Bromoform	234.9	Ethylene Diamine	10,440.9
Dichlorodifluoromethane	376.0	Furfural	10,492.6
Carbon Tetrachloride	436.7	Nitrobenzene	10,819.8
Hexachloroethane	836.5	Ethyl Acetate	10,984.4
Chloroform	1,345.2	Methyl Methacrylate	11,143.3
Tetrachloroethylene	2,142.5	Paraldehyde	11,342.3
1,1,1,2-Tetrachloroethane	2,502.6	Ethanal	11,381.0
1,1,2,2-Tetrachloroethane	2,502.6	Ethyl Acrylate	11,785.9
Methylene Chloride	3,063.5	1,4-Dioxane	11,887.0
Trichloroethylene	3,132.8	Oxirane	12,338.9
Methyl Bromide	3,486.8	Acrolein	12,524.8
Bis(chloromethyl)ether	3,546.9	Acetonitrile	13,278.4
1,1,1-Trichloroethane	3,582.8	Acetone	13,282.9
1,1,2-Trichloroethane	3,582.8	Ethylenamine	13,433.5
Methyl Chloride	5,185.4	Allyl Alcohol	13,711.2
Chloroacetaldehyde	5,257.3	Methyl Ethyl Ketone	14,587.2
Ethylidene Dichloride	5,401.0	Cresols	14,709.9
1,1-Dichloroethylene	5,401.2	2-Picoline	14,903.3
1,2-Dichloroethylene	5,401.2	Dimethylamine	14,907.2
Carbon Disulfide	5,841.9	Pyridine	15,155.3
Chloromethyl Ethyl Ether	5,947.7	Isobutyl Alcohol	15,526.8
Ethylene Dichloride	6,165.8	1-Butanol	15,559.4
1,3-Dichloropropylene	6,193.3	Aniline	15,712.9
1,2-Dichloropropane	7,184.0	Ethyl Ether	15,857.1
Acrylic Acid	8,170.1	n-Propylamine	17,217.8
Formaldehyde	8,179.0	Benzene	17.998.0
Epichlorohydrin	8,224.1	Toluene	18,246.0
m-Dichlorobenzene	8,227.2	Ethyl Benzene	18,505.8
Methyl Isocyanate	8,509.4	Xylenes	18,523.2
2-Nitropropane	9,667.2	Cumene	18,683.8
Methanol	9,769.1	Cyclohexane	20,080.1

Source: Refer to Appendix A.

systems. T_{99} is dependent on residence time.[11(e)] Analysis of pooled field test data has indicated that no strong correlation could be found for DRE as opposed to any of the thermal ranking methods. Research data, however, suggest the use of an incinerability ranking based on gas-phase thermal stability data collected in laboratory experiments under oxygen deficient conditions.[11(e)]

Comparison of these stabilty data with appropriate field test data indicates that field thermal stabilty rankings could be predicted from the laboratory data in 70 percent of the cases evaluated. Additional research is being conducted to expand the number of compounds for which comparisons can be made.

Indication parameters, including the Arrehenius coefficient and activation energy parameters used to establish the reaction rate coefficient previously discussed, are presented for several of the solvent hazardous wastes in Table 10.2.

Moisture Content--

Moisture contained in the waste reduces the incinerability of a waste. In the combustion process, water will absorb heat energy and vaporize, but will not oxidize or pyrolyze. This will tend to reduce the heat energy available to assist the combustion. Water may also absorb combustion intermediates and waste components and thus limit their availability for combustion.

The requirement to drive off moisture increases the overall stress on incineration systems, and increases the operating costs. Certain incinerator design, including fixed hearth furnaces and rotary kilns, are not equipped to handle high moisture content wastes. Moisture content may be reduced by dewatering pretreatments, but these tend to be expensive.[13] The most common way of dealing with high moisture content wastes is to blend them with solid wastes or other high heat content materials.[14]

TABLE 10.2. CHARACTERISTIC PARAMETERS FOR SEVERAL SOLVENT HAZARDOUS WASTES

Compound	A	E (cal/g-mole)	Autoignition temperature (AIT) (°F)	(TLL) lower limiting temperature for incineration (°F)	Estimated temperature for 99.99% destruction (T99)	
					At 1-second residence (°F)	At 2-second residence (°F)
Acrolein	3.3×10^{10}	35,900	453	800	1,020	975
Athyl alcohol	1.75×10^{6}	21,400	713	1,050	1,176	1,072
Athyl chloride	3.89×10^{7}	29,100	905	1,150	1,276	1,200
Benzene	7.43×10^{21}	95,900	1,044	1,275	1,351	1,322
(mono) chlorobenzene	1.34×10^{17}	76,600	1,180	1,350	1,408	1,372
1,2-Dichloroethane	4.8×10^{11}	45,600	775	1,050	1,216	1,173
Ethanol	5.37×10^{11}	48,100	793	1,250	1,307	1,256
Ethyl acrylate	2.19×10^{12}	46,000	721	1,000	1,132	1,092
Methyl chloride	7.34×10^{8}	40,900	1,170	1,500	1,597	1,514
Methyl ethyl ketone	1.45×10^{14}	58,400	960	1,200	1,290	1,247
Toluene	2.28×10^{13}	56,500	997	1,275	1,340	1,295
Vinyl acetate	2.54×10^{9}	35,900	800	1,150	1,223	1,164
Vinyl chloride	3.57×10^{14}	63,300	882	1,250	1,371	1,332

Source: Lee et al., June 1982 (Reference 12).

Ash Content (Solids/Metals/Thermally Inert Materials Content)--

The ash content of a hazardous waste is considered a very important incinerability indicator. Ash content is defined here as that portion of a waste which is either a noncombustible solid or will form a solid byproduct in the combustion process. Ash content, therefore, encompasses most of the suspended solids, metals, and other (primarily inorganic) thermally inert compounds of a waste (it is important to note that some solids will combust readily in the process).

Ash content directly impacts both the overall combustibility of a waste and the materials handling requirements both before and after the combustion stage of the process. Wastes with higher ash contents tend to be more difficult to pump, and will tend to plug liquid atomizers more readily. Ash components are more difficult to disperse and require more energy input in handling. Higher ash contents increase the possibility of unburned waste carryover to the recovered ash stream. Particularly in the case of high heavy metals content, higher ash contents may lead to higher emissions of particulate matter or pollutant particles of concern.[15]

Ash content is used to determine the type of incinerator selected, air pollution control equipment required, ash recovery system required, and is often directly used in incineration pricing structures. Rotary kiln and hearth type incinerators are, in general, more applicable to wastes with higher ash content, while liquid injection and fluidized-bed incinerators are less applicable. Fluidized-bed incinerators have a particular limitation to wastes containing sodium salts which tend to clog the bed, leading to process failure.[16] The costs of incinerating wastes with higher ash content are higher primarily due to increased air pollution control and ash recovery costs. Many incineration facilities appear to use ash content as a factor in determining the price of incinerating wastes. One facility contacted, for example, indicated that they charged an extra 1 cent per pound per each percent of ash content.[17] Solvent hazardous wastes generally have low ash contents. An example of the ash contents of a variety of solvent waste streams is shown in Table 10.3.

TABLE 10.3. WASTE CHARACTERISTIC DATA FOR SEVERAL SOLVENT HAZARDOUS WASTE STREAMS

Waste description	EPA waste code	Ash content (%)	Chlorine content (%)
Trichloroethylene spent solvent waste	F001, F002	2	65
1,1,1-Trichloroethane spent solvent waste	F001, F002	2	64
Methylene chloride spent solvent waste	F001	2	33
Tetrachloroethylene spent solvent waste	F002	2	68
Spent degreasing solvents from electroplating metal cleaning	F001	2	46
Degreaser sludge from electroplating metal cleaning	F001	20	32
Spent solvents, N.O.S.	F004, F005	2	0
Trichloroethylene still bottoms	F001, F002	0	16
1,1,1-Trichloroethane still bottoms	F001, F002	20	16
Methylene chloride still bottoms	F001	20	8
Still bottoms, N.O.S.	F004, F005	20	0

Source: W-E-T Model Hazardous Waste Data Base, 1982 (Reference 18).

Chloride Content--

The chloride content of a waste is also considered a very important indicator for incineration. Chloride content relates directly to the formation of HCl and possibly Cl_2 gas. The emission of both of these compounds is regulated by environmental standards and, thus, most wastes containing more than nominal levels of chloride require air pollution controls. The chloride concentration is also related to the overall corrosivity of combustion byproducts. As a result, most incinerators establish a limiting chloride concentration for their systems. It is common for this limit to fall under 3 percent by weight. Most incinerators also appear to have established surcharges for chloride content. One facility contacted stated that an additional charge of 0.2 cents per pound per each 1 percent of chloride was common practice in the industry.[17]

Some solvent hazardous wastes, as shown in Table 10.3, are halogenated organics and the chloride content of those wastes is often extremely high. Assuming the total conversion of all chlorine within the waste to HCl, the concentration of HCl in the exit gases under normal combustion can approach 1 $gram/m^3$ of flue gas for a waste containing 2 percent chlorine. This estimate assumes that the molecular structure and heating value of the waste or a waste/fuel mixture approaches that of a No. 2 or No. 6 fuel.

Viscosity--

The viscosity of a waste impacts its pumpability and atomization, and must be considered if incineration in a liquid injection unit is contemplated. Liquid injection incinerators will require that wastes be atomizable to be effectively destroyed and, therefore, must operate within a general viscosity limit.[13] Although the limit varies, depending on characteristics of the waste burned and the injection system design, the usual limiting range falls between 50 and 200 SSU. Viscosity also may somewhat limit the applicability of wastes to fluidized-bed or multiple hearth incinerators. Fluidized-bed incinerators require that liquid wastes be "pumpable" in order to be effectively dispersed in the bed. A common "pumpability" limit is 10,000 SSU at 100°F and assumes that the viscosity will be at an acceptable level for atomization when heated. Multiple hearth incinerators require that a liquid be dispersed by an impeller mechanism for effective performance. Highly viscous wastes are not well dispersed by such mechanisms, and they actually may flow through a multiple hearth too rapidly for effective destruction (commonly falling directly to the ash recovery conveyor).

Highly viscous wastes are commonly subjected to preheating or blending with more mobile, compatible solvent wastes.

Corrosivity--

Corrosivity directly impacts upon equipment design and costs, and materials handling requirements. Certain incinerator designs may not be appropriate for highly corrosive materials. In particular, fluidized-bed materials and metal parts can be affected by corrosivity. In general, pretreatment methods (e.g., chemical neutralization) should be employed before incinerating corrosives.

10.1.3 Strategy for Assessment of Incinerability

As stated by Martin and Weinberger, incineration is a potential option for the disposal of all hazardous waste.[3] Although no one type of incinerator exists that can effectively destroy all types of hazardous wastes, there is likely to be at least one type of incinerator capable of burning any particular type of waste. Once it has been established that no technological options exist which may more effectively or economically manage a waste, a strategy should be adopted to determine the best incineration technology to handle the material. This strategy should be based upon waste characteristics. A recommended approach, based upon the strategy designed in Reference 3, is outlined below:

1. Determine whether the waste can be physically introduced to the combustion zone as is, or if pretreatment is required. This determination is based upon physical form and viscosity. For example, if the waste is a liquid with low viscosity, it can be atomized and, thus, may best be input through a liquid injection system.

2. Determine the overall physical effect of the waste on the incineration system. This consideration is primarily based upon the physical form, solids content, and corrosivity of a waste. These factors may be such that the incineration of the waste will rapidly lead to process failures due to debilitation of equipment. Refractory linings, for example, are highly susceptible to chipping and cracking by large solid particles.

3. Determine if auxiliary fuel should be used. This determination is commonly made solely on the basis of the heat of combustion. For example, wastes with a heat of combustion of below 2,500 Btu/lb are almost always mixed with a fuel or blended with a high Btu waste.

4. Determine the temperature and residence time requirement for effective combustion. This determination is largely based on characteristics such as moisture content. Many incinerator designs operate with a specified time or temperature range, while waste feed rate may be adjusted.

5. Determine the disposal or handling method required for combustion byproducts other than gaseous products. This consideration is largely based upon the solid/metal/thermally inert material concentration of the waste. Wastes with a high ash concentration, for example, may require a continuous ash removal system.

6. Determine if air pollution controls are required. This consideration is largely based upon the chloride and ash content of a waste. Most wastes containing more than a very small amount of chloride will require a scrubber to remove acid gases. Need can be calculated assuming emissions are directly related to input.

7. Determine if relevant environmental standards can be met. This determination, again, is based upon chloride and/or ash concentration. Most incinerators operate with a chloride concentration limit. If the chloride content is too high, the air pollution control system will not be adequate to limit emissions to the applicable standard.

8. Determine overall costs of incinerating the waste. After considering all of the factors detailed above, the relative costs associated with these technologies should be estimated. It is important to note that the technology with the lowest base cost may not be the most cost-effective alternative, should one of the factors listed above come significantly into play.

A flow chart detailing the general considerations to be made in selecting the appropriate incineration system. This flow chart is presented in Figure 10.1.[3]

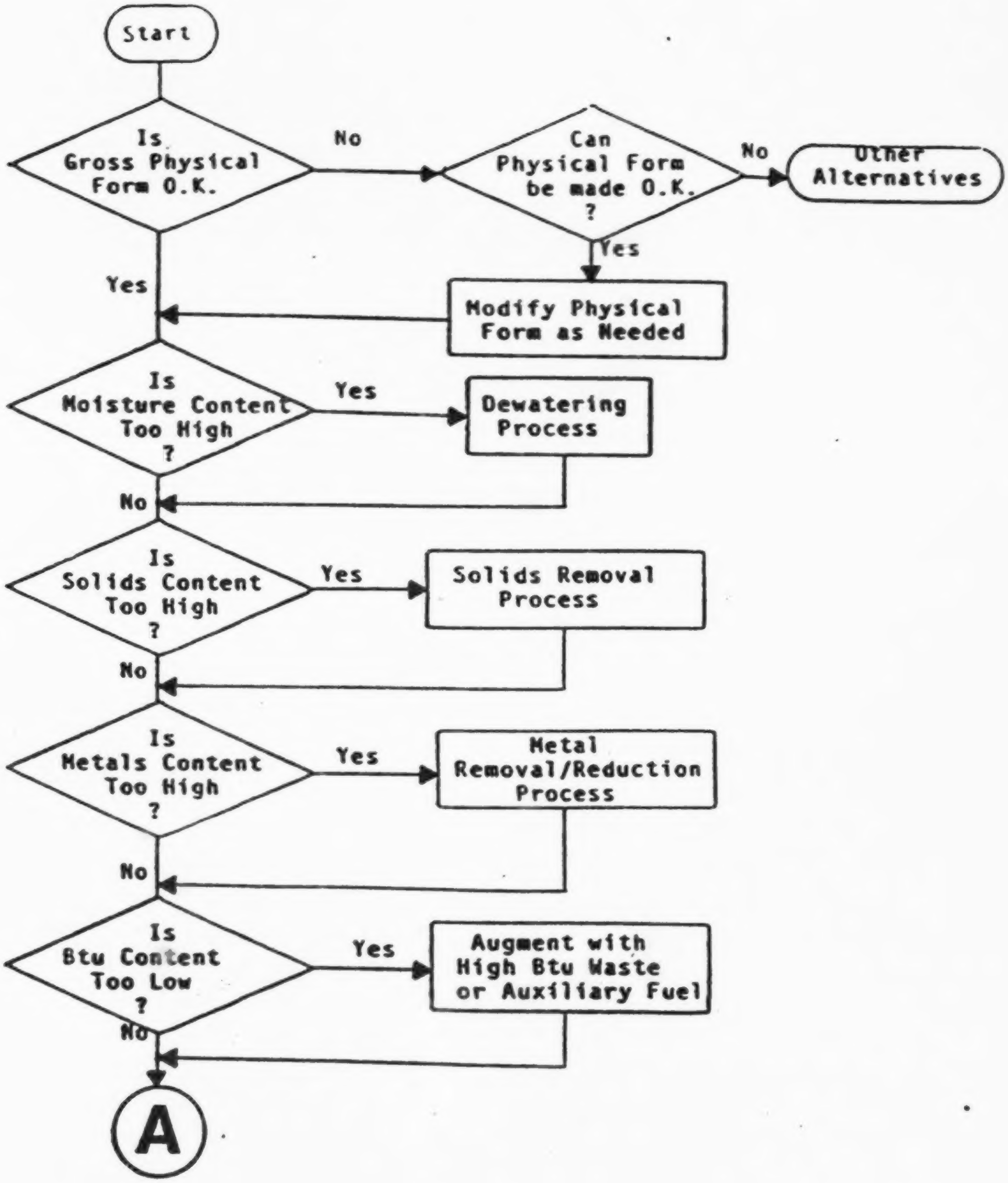
Start
Is Gross Physical Form O.K.
No
Can Physical Form be made O.K. ?
No
Other Alternatives
Yes
Yes
Modify Physical Form as Needed
Is Moisture Content Too High ?
Yes
Dewatering Process
No
Is Solids Content Too High ?
Yes
Solids Removal Process
No
Is Metals Content Too High ?
Yes
Metal Removal/Reduction Process
No
Is Btu Content Too Low ?
Yes
Augment with High Btu Waste or Auxiliary Fuel
No
A

Figure 10.1. Pretreatment option logical decision flow chart.

Based on the "standard" measures employed to evaluate the incinerability of hazardous wastes, solvent hazardous wastes are generally considered good candidates for incineration. The characteristics which appear to give solvent hazardous wastes good incinerability include the following:

- Most solvent hazardous wastes are found in the liquid form. Liquid wastes tend to burn more efficiently because they are easily dispersed and, thus, mix more readily with combustion air;
- Most solvent hazardous wastes are composed primarily of organic materials; (i.e., they contain low levels of solids and inert materials) which oxidize or pyrolyze more readily;
- Solvent wastes often can be blended with many other types of wastes to render them applicable to a wider range of technologies; and
- Solvent wastes do tend to have high Btu values and relatively low autoignition temperatures, indicating that they are more readily combustible.

Solvent hazardous waste characteristics which limit their applicability to incineration include:

- Air pollution control requirements because chlorine and ash concentrations can be high; and
- More pretreatment requirements for some solvent hazardous wastes than for other types of wastes.[10]

In addition, low flash point wastes may require processing or blending to reduce the potential hazards related to storage and combustion of these materials.

10.2 PROCESS DESCRIPTION

There are numerous incineration system designs available to handle the wide variation of chemical and physical characteristics found in hazardous wastes. Hazardous waste incineration technologies range from those with widespread commercial application and many years of proven effective performance, to those currently in development. As many as 67 companies may be involved in the design and development of hazardous waste incinerators,[20] with more expected as limitations on land disposal of hazardous wastes increase.

As mentioned previously, there are several incineration technologies which have become established commercially as the primary options available for the incineration of hazardous wastes. These technologies have been demonstrated extensively for a wide range of hazardous wastes. They comprise about 80 percent (by number) of the U.S. market.[19(a),20] They include:

Liquid injection incineration

Rotary kilns

Fluidized-bed incinerators

Fixed hearth incinerators, particularly the starved air or pyrolysis type units, and

Multiple hearth incinerators.

The first two (and the fixed hearth units) are the most widely used for the disposal of hazardous wastes. A description of the first three types of units listed above will be provided here, following a brief description of basic components common to all incinerators. The hearth type incinerators, particularly the fixed hearth unit, are also used extensively, but data on their ability to handle hazardous wastes have not been widely published in the literature. Discussions of the design and operation of these systems can be found in the open literature.

All incineration systems are designed in consideration of the four basic elements of combustion: temperature, time, turbulence, and concentration, as described previously. Temperature is the most important element of an incineration system.[21] The heat requirements govern the method in which heat energy is supplied and sustained within the combustion chamber, and governs many of the pretreatment operations conducted. Residence time requirements impact the size of the combustion chamber, as the volume of the combustion zone must be sufficient to allow for completion of thermal destruction. Turbulence is strictly a function of incinerator design. Elements such as baffles, rotation, or changes in direction within the combustion chamber increase turbulence (and, therefore, enhance mixing of wastes and oxygen to allow for more effective performance). Concentration governs the oxygen input requirement, as sufficient air must be supplied to insure complete combustion of hazardous constituents.

In terms of the chemical process system, there are essentially five component parts common to any incineration facility, as shown in Figure 10.2 and discussed below.

1. Material Storage and Preparation--Waste materials are received, analyzed, stored and prepared for input into the incinerator. In this initial step of the incineration process, the waste characteristics which may affect the performance of the incinerator are identified. If necessary, pretreatment operations are conducted to mitigate these characteristics. In some cases, wastes are rejected for incineration when pretreatment will not render them "incinerable" in the technology present.

   Common methods of pretreatment include preheating, chemical neutralization, filtration/sedimentation of suspended solids and water, and distillation. Many of these technologies are described in detail in other sections of this document.

2. Waste Feed Mechanism--The waste feed mechanism is not merely the means by which waste materials are input into the combustion chamber of an incinerator. Feed mechanisms control the volume of waste present in the chamber at any moment, and thus control waste residence time. Feed mechanisms also play a key role in creating surface area to increase combustion rate and developing turbulence within the combustion system. Dispersion of wastes is particularly critical in liquid injection and fluidized-bed incinerators.

3. Combustion System--As described previously, combustion systems perform three functions: 1) heating of waste materials to vaporize and pyrolyze them; 2) mixing of wastes with combustion air; and 3) oxidation and subsequent formation and separation of combustion products.

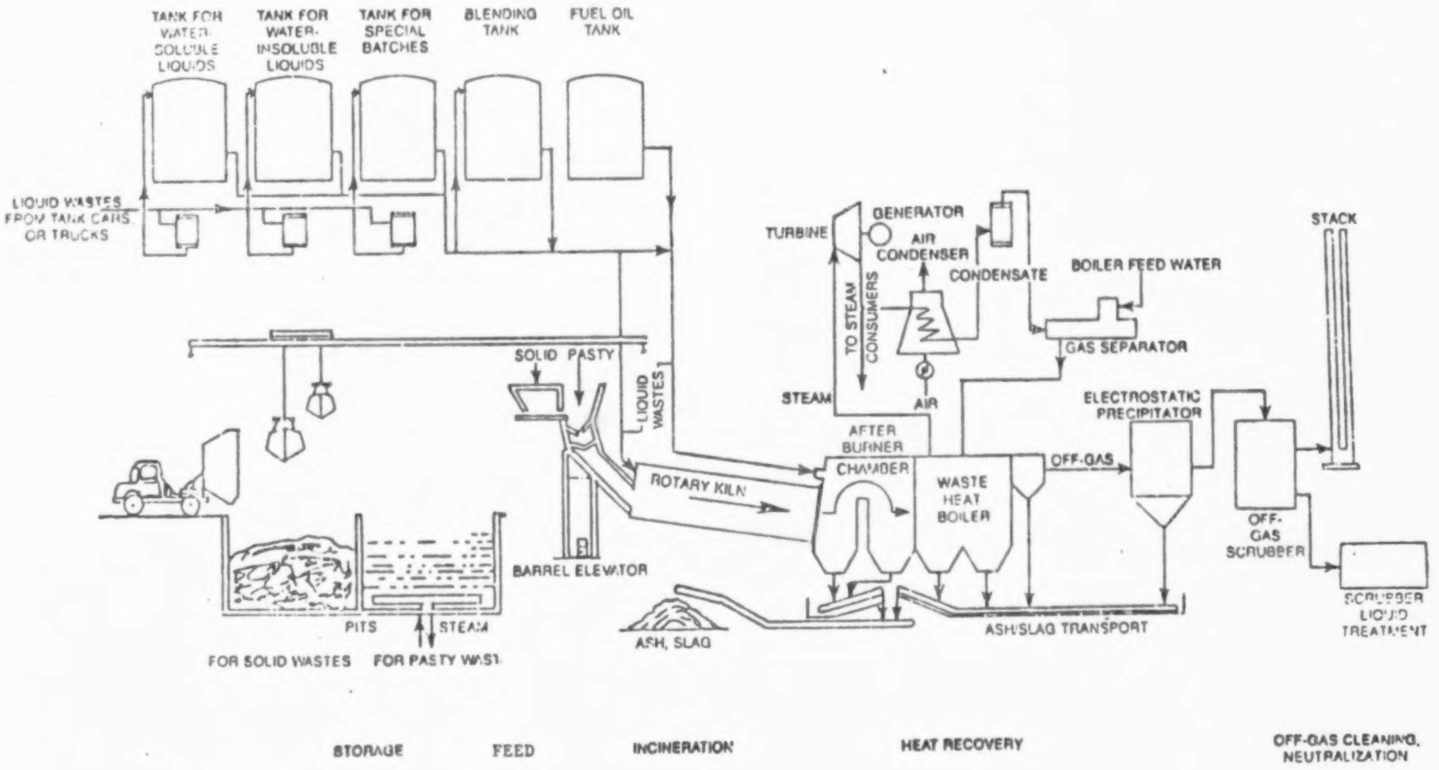

Figure 10.2. Flow sheet of an incineration plant for hazardous wastes.
Source: Babcock Krauss-Maffei Industrieanlagen GMBH
(Revised by P. Adie)[22]

4. Heat Recovery--Heat recovery systems are often employed with incineration of hazardous wastes in order to achieve greater cost effectiveness of the operation as a whole. Generally, heat recovery is accomplished by either standard type heat exchange equipment or waste heat boilers which burn the waste byproducts. There are generally two limitations in heat recovery. First, the cost benefits of heat recovery must justify the expense of the heat recovery system, including design, installation, and maintenance. Second, heat recovery systems should not be used if they lead to a more difficult waste management problem (i.e., form new pollutants of concern, or require difficult maintenance, e.g., cleanup of waste byproducts plugging the heat recovery system).

5. Solid and Liquid Waste Control--Air pollltion control devices and air pollution control systems are required if the combustion process produces air pollutants at levels exceeding applicable emissions standards. Most commonly, the primary pollutants of concern generated by incineration of hazardous wastes are particluate matter and hydrochloric acid (HCl) vapor. Air pollution control is often but not always used at hazardous waste incinerators. Incineration processes produce solid and liquid waste streams which must be managed. These streams are usually not hazardous themselves. Ash produced in combustion is collected either continuously by some mechanism; e.g., a screw conveyor built into the bottom of the combustion system, or periodically by manually cleaning the combustion chamber. Sludges can be produced by air pollution control or heat recovery systems, and are removed periodically from the process systems. Liquid wastes produced by air pollution scrubbers or quench towers are continuously treated. In most cases, ash may be disposed of in a landfill, as may dried sludges. Liquid wastes may be subject to waste water treatments before discharge.

10.2.1 Liquid Injection Incinerators

Liquid Injection (LI) incinerators are the most widely used hazardous waste incineration system in the United States, accounting for 64 percent of the total number of hazardous waste incinerators in use in the U.S.[20] LI systems may be used to incinerate virtually any liquid hazardous waste, including most solvent hazardous wastes, due to their very basic design and high temperature and residence time capabilities. Liquid injection incinerators represent the most effective system available for most liquid hazardous waste solvents, from both a technical; (i.e., destruction efficiency) and economic perspective.

Liquid injection incinerator systems typically employ a basic, fixed hearth combustion chamber. Pretreatment systems to blend wastes and fuels, to remove solids and free water, and to lower viscosity through heating, are often used in conjunction with liquid injection incinerators. Ash recovery systems may not be required, at least on a continuous basis, because many liquid hazardous wastes fired in an LI system contain low volumes of ash or suspended solids.[9]

The liquid waste feed system is the key element of the LI process. Liquid injection incinerators operate as "suspension burners", whose combustion efficiency (and hence destruction efficiency for constituents of hazardous wastes) is dependent upon the extent to which the feed mechanism can disperse the liquid waste within the combustion chamber and provide sufficient area for contacting waste with combustion air. There are two atomizer designs commonly employed in LI systems, denoted as fluid systems and mechanical systems. Typical characteristics of several atomizer designs are described in detail in Reference 23.

Once liquid wastes enter into the liquid injection incinerator and are ignited at the burner, the turbulence imparted to the waste and good mixing with combustion air lead to efficient combustion. Combustion temperature capabilities of the systems can be very high, reaching over 3,000°F in many cases. Residence times are generally within a 1 to 2 second range, depending upon liquid heat content.[13] Table 10.4 summarizes operating parameters for typical hazardous waste liquid injection systems.

Applicability of hazardous wastes to liquid injection incinerators is generally limited by the extent to which they may be atomized, and the physical effect they may have on the incinerator equipment (mostly notably, on the atomizer). The primary restrictive waste characteristics of interest are the liquid viscosity, solids content, and corrosivity. Wastes with low heat value may also be restricted from burning in a liquid injection incinerator. A typical limiting value (below which waste must be mixed with a fuel, or a high heat value material), given by one incinerator operator, is 5,000 Btu/lb.[24]

TABLE 10.4. OPERATING PARAMETERS OF HAZARDOUS WASTE LIQUID INJECTION INCINERATORS

Form of waste feed:	• Liquid wastes only. • Limiting liquid viscosity for atomization is typically 16,000 centistokes. • Limiting solids content may be as high as 10% by weight undissolved solids. • Limiting solid particle size may be as high as 1/8-inch diameter.
Heat input capacity range:	5 to 150 x 10^6 Btu/hr.
Heat release:	25,000 Btu/hr.ft^3 (typical) 1,000,000 Btu/hr.ft^3 (maximum)
Operating temperature range:	1,200 to 3,000°F
Residence time range:	0.5 to 2.0 seconds
Excess air:	20% (typical) For nitrogen-containing wastes, excess air requirements may be 65 to 95%.
Pressure:	0.5 to 4 in. H_2O (typical)

Source: MITRE, 1982 (Reference 20).

Liquid viscosity is regarded as the primary limiting waste characteristic for liquid injection systems since viscosity determines whether or not the liquid is pumpable and atomizable. Pretreatment may be needed to reduce the viscosity of wastes to a level where high combustion efficiencies may be achieved. The two most common viscosity reducing pretreatment operations are heating and dilution. In some cases, high energy mixing is done to produce a one- or two-phase emulsion of liquid waste in the carrier media. Energy for preheating is often supplied by heat recovery systems.

Suspended solids are another restrictive waste characteristics for liquid injection incinerators. Undissolved solids can impact negatively through abrasion or plugging. The best available technology to reduce the solids content is filtration or sedimentation. Filtered solids may be collected, washed of any retained liquids by an appropriate solvent, and disposed of separately. Wash solutions can be incinerated.

Highly corrosive wastes provide a potential limitation to effective performance of liquid injection systems. However, no pH limits for liquid injection incineration were described in the available literature other than those dealing with chloride content, and no detail was provided on chemical pretreatment of corrosive wastes. It can be assumed that such techniques are viable for LI systems, however, depending on the characteristics of wastes handled and process design.

In some cases, the applicability of an LI incinerator may be extended by the use of multiple injection systems. In this way, an injector may be fitted to more specific ranges in waste characteristics allowing a broader range of overall usage without requiring pretreatment. As discussed earlier, certain atomization device designs are better suited to more viscous or higher suspended solids containing wastes than others. In addition, the use of multiple injection points may allow for concineration of incompatible wastes.

10.2.2 Rotary Kiln Incinerators

Rotary kiln (RK) incinerators have found widespread application in the U.S. for management of hazardous wastes, both at chemical manufacturing and at hazardous waste facilities.[19] MITRE estimated that rotary kilns comprised

12.3 percent of the total number of hazardous waste incinerators in operation.[20] Rotary kiln systems are considered the most versatile of the established incinerator technologies. Liquid, solid, and slurried hazardous wastes may all be burned in rotary kilns, without extensive adaptation of the design for specific waste types.

Rotary kiln systems employ a fairly basic design concept. As depicted in Figure 10.3, the typical rotary kiln system involves two-stage combustion of waste materials with primary combustion occuring in the rotary kiln followed by secondary combustion of gaseous byproducts. Heat recovery, ash recovery, and air pollution control devices are usually included in the overall system. Combustion byproducts are most often scrubbed for both particulate matter and acidic byproducts; e.g., HCl. Heat recovery is employed in the majority (70 percent, according to recent estimates) of cases.[20]

Pretreatment of hazardous wastes is not often required for incineration in a rotary kiln, because of the great versatility of the system. The most common preparatory operations conducted at rotary kiln incinerators include size reduction, mixing of liquid wastes with solid wastes, and chemical neutralization. Wastes with an average heating value of 4,500 Btu/lb are reported adequate to sustain combustion at kiln temperatures between 1,600 and 1,800°F.[20] In those cases where auxiliary fuel is required, No. 2 fuel oil is used most often.[20] Size reduction of solid waters, via crushing and grinding operations, is a common preparatory operation. This is often done both to preserve the life span of the kiln refractory lining and to increase the combustion efficiency of the system. Mixing of liquid wastes with solid wastes helps to increase the liquid waste residence time and thus enhance destruction efficiency. Highly corrosive wastes are often neutralized by chemical treatment before being fed to the rotary kiln. This helps preserve the working life of the kiln refractory.

Waste materials, following pretreatment, are fed to the elevated end of the rotary kiln. Waste feed mechanisms employed are typically simple hoppers which feed a regulated amount of material to the kiln. Vendors generally recommend continuous operation of a rotary kiln, although they may be operated

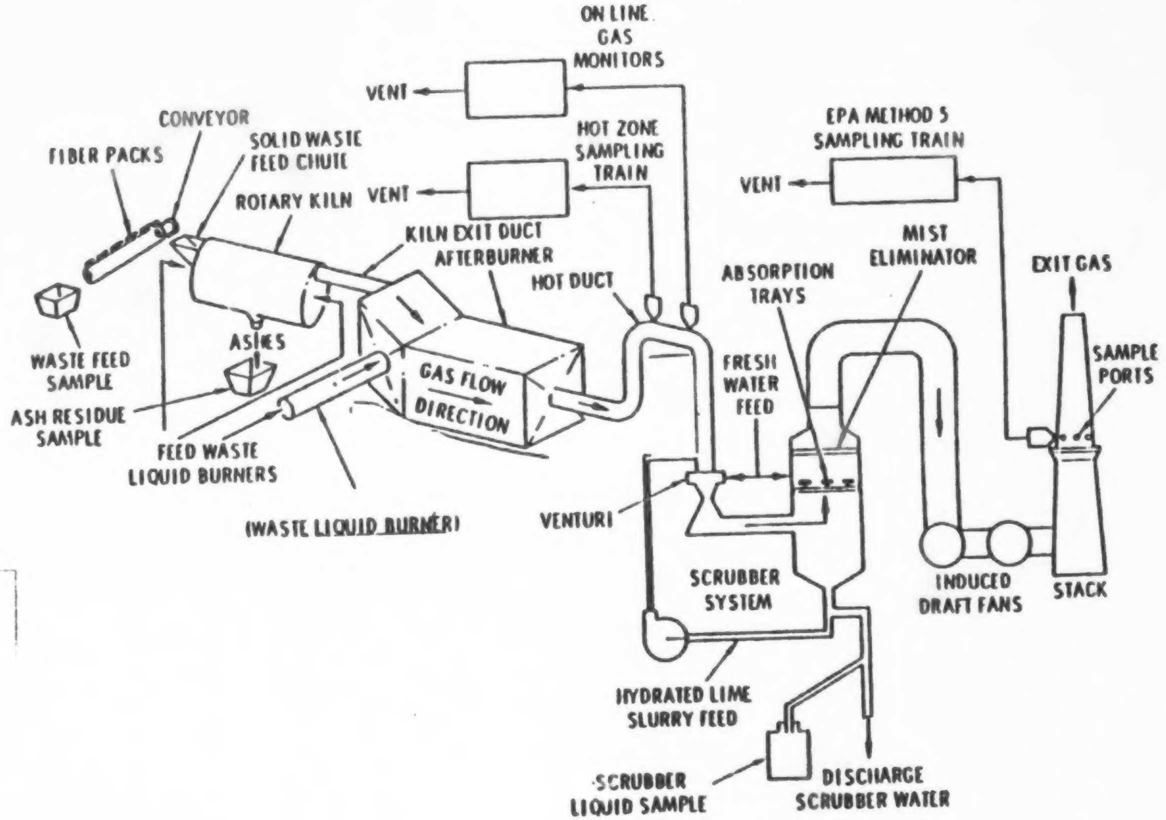

Figure 10.3. Rotary kiln incinerator with liquid injection capability.

intermittently.[25] Waste materials flow through the rotary kiln as a consequence of the rotation and the angle of inclination. The kiln is often designed with baffles, which serve to regulate the flow rate through the unit, generally resulting in increased residence times. The rotation of the kiln serves to enhance the mixing of waste with combustion air and provides continuously renewed contact between waste material and the hot walls of the kiln. Combustion air is fed either concurrently or countercurrently. One feature of a rotary kiln is that it may be operated under substoichiometric (oxygen deficient) conditions to pyrolyze certain wastes.

As combustion of the waste progresses, ash flows to the bottom of the unit and is conveyed the ash recovery system. Gaseous combustion products are exhausted to the secondary combustion unit.

Secondary combustion generally takes place in a fixed hearth type unit, where gaseous products of combustion, including incompletely combusted waste components, combustible waste products, and fly ash are fired. The gaseous products from the secondary combustion chamber are normally then passed through heat recovery and air pollution control systems, while ash is collected and transported to the ash recovery facility.

Most rotary kiln systems are equipped with a multistage scrubber system to control particulate matter, acid byproducts of combustion, and oxides of sulfur and nitrogen. Heat recovery systems are often used not only for the conservation of energy, but also to reduce temperatures to allowable levels prior to introduction to the scrubbers. Typical operating parameters for a rotary kiln system are shown in Table 10.5.

Rotary kilns are generally large systems, and thus require a large capital expenditure. Due to their energy requirements, the operating costs associated with rotary kiln systems may also be higher than other incinerator system. Their versatility may lead, however, to benefits measurable in overall reduced costs for hazardous waste management; cost considerations are further discussed later in this section.

TABLE 10.5. OPERATING PARAMETERS FOR ROTARY KILNS

Form of wastes fed:	Liquid, solid, slurry. Virtually any waste may be fired in a rotary kiln.
Thermal capacity:	1 to 150 x 10^6 Btu/hr (rotary kiln) 20,000 Btu/hr (secondary combuster)
Typical overall system flowrate:	
Gas flow	47,000 ACFM at 2,200°F
Pressure drop	10 to 25 in H_2O
Solid feed rate	10,000 lbs/hr
Liquid feed rate	3,000 lbs/hr
Combustion temperature:	
First chamber (rotary kiln)	500 to 2,300°F
Second chamber	1,600 to 2,800°F
Residence time:	
Gases	0.5 to 3.0 seconds
Solids	Highly variable, depending on viscosity, angle of inclination, and rotation of kiln.
Rotational speed:	12 revolutions/hr (typical)
Length to diameter ratio:	10:2 (typical)
Excess air:	60 to 150 percent
Refractory life:	24 to 30 months

Source: MITRE, 1982 (Reference 20).

10.2.3 Fluidized-Bed Incinerators

Fluidized-bed (FB) incineration systems represent a newer incineration technology which has not yet made a significant commercial impact in the established incinerator market. Although fluidized-bed processing units were developed nearly 50 years ago and have found extensive application both in chemical processing, and more recently, in sewage sludge incineration, the development of FB systems capable of destroying wastes containing hazardous components is still in its early stages. As indicated in MITRE's 1982 survey,[20] only nine fluidized-bed units, representing 2.6 percent of the total number of hazardous waste systems in operation, had been put into actual service at hazardous waste processing facilities. The basic fluidized-bed system, as depicted in Figure 10.4, consists of a refractory-lined vessel; a perforated plate which supports a bed of granular material and distributes air; a section above the distributor containing granular solids referred to as the freeboard; an air blower to move air though the unit; a cyclone to remove particles and return them to the fluidized bed (not shown in Figure 10.4); an air preheater; a start-up bed heater; and a system to inject and distribute the feed in the bed. Fluidized-beds are always oriented vertically. Feed and air flow are balanced to achieve fluidization in the bed. The fluidized-bed promotes turbulence and serves as an excellent heat transfer medium, thus assisting combustion. As will be discussed later, the fluidized-bed material can be chosen to react directly with combustion production such as HCl, thus minimizing subsequent air pollution control requirements.

Fluidized-beds are capable of burning all forms of waste, and due to the high turbulence present, no atomization is required. Combustion air and auxiliary fuel are introduced from the bottom. The bed is kept at a high temperature (typically, between 1,250 and 1,750°F), so the waste materials almost immediately will begin to burn as they mix with the fluidized-bed. The gaseous products of combustion flow out the top of the incineration units, to be scrubbed and passed through heat exchangers for heat recovery. The solid products either remain within the fluidized-bed if they

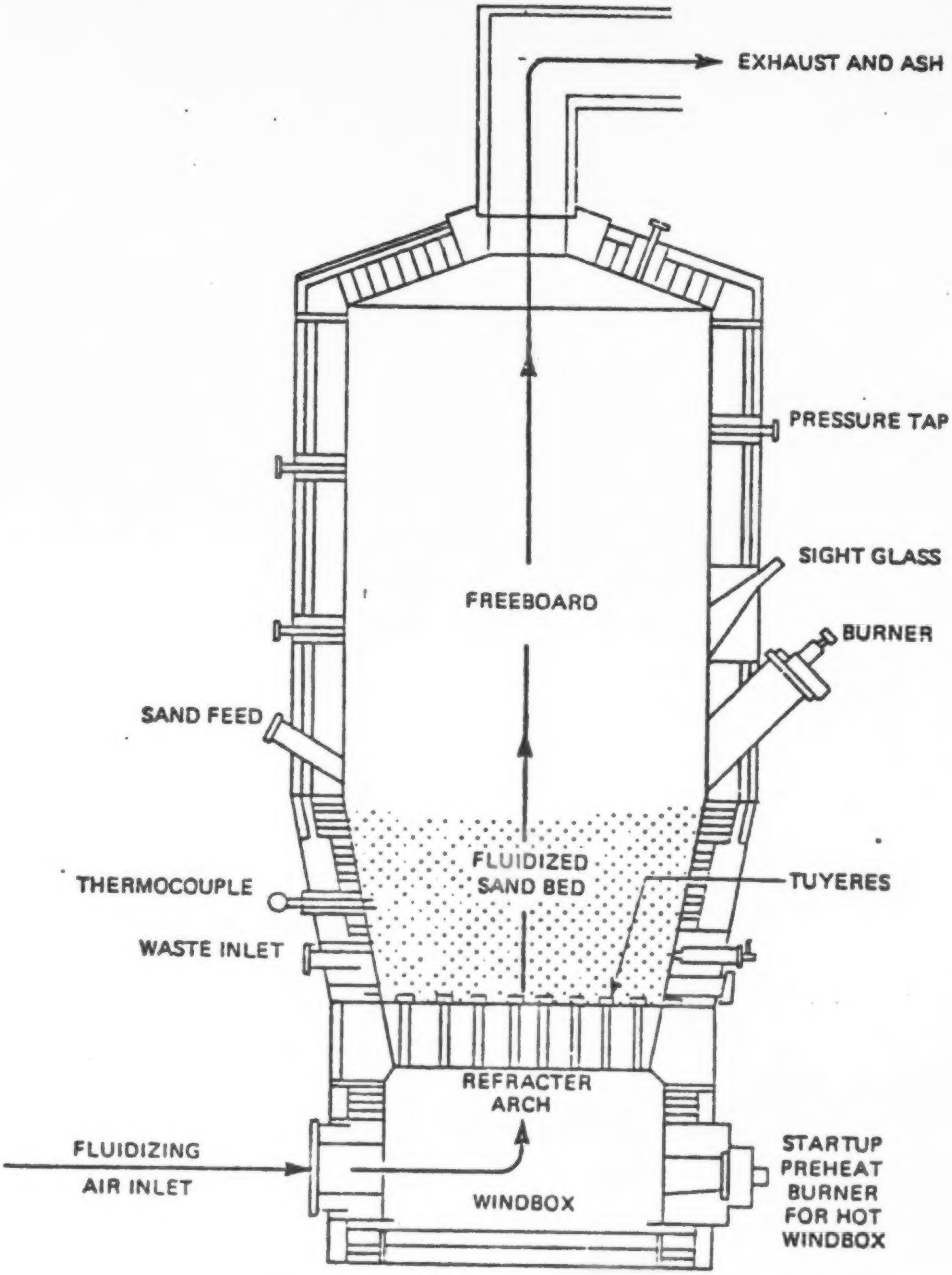

Figure 10.4. Cross-section of a fluidized-bed furnace.
Source: Reference 22.

are of approximately equal mass to the bed particles, fall to the bottom of the bed where they will eventually be removed by the ash recovery system, or become entrained in the exit gases, where they will be removed by the air pollution control system.

Operating parameters for fluidized-bed incineration are shown in Table 10.6. As shown in the table, operating temperatures are lower than those found in other types of incinerators. However, the long residence times and the excellent distribution of thermal energy within the bed are sufficient to provide excellent destruction efficiency of organic solvents.

The usage of a fluidized-bed incinerator may be limited, by certain chemical characteristics of a hazardous waste. In general these restrictive waste characteristics are those properties which may affect the fluidity of the bed itself. The key to the effectiveness of an FB incinerator is the ability of the bed to display certain liquid-like physical properties. Those wastes with characteristics which lead to either an increase or decrease in bed particle mobility are not suitable for FB incineration. The primary waste characteristics identified as potentially restrictive include sodium content, corrosivity, moisture content, and fusable ash content.

Sodium content has been identified as the most significant property of concern, in determining the applicability of fluidized-bed incinerators to the treatment of a facility's hazardous wastes. Certain sodium salts, most notably sulfates and nitrates, may form eutectic complexes with other inorganic salts present in the bed which serve to bind bed particles together, and thus destroy the fluidity of the bed.[25]

Highly corrosive wastes pose a different threat to the integrity of the fluidized-bed. The fluidity of the fluidized-bed are dependent upon maintenance of a certain bed particle density and size distribution. Thus, reactions which alter these properties are detrimental to the effective operation of the bed. Corrosion of the bed may therefore lead to a loss of fluidization and result in significantly lower destruction efficiencies achievable by the system.

Wastes with very high moisture content may reduce the overall effectiveness of the fluidized-bed system. Wastes containing more than 75 percent moisture, by weight, may require temperatures or residence times

TABLE 10.6. OPERATING PARAMETERS OF FLUIDIZED BED INCINERATORS

Feed materials:	Granular solids, sludges, slurries are best but can handle liquids, bulk solids, as well.
Capacity:	2 to 200 x 10^6 Btu/hr heat input.
Operating temperature:	1,600 to 1,850°F in combustion zone.
Residence time:	
Gaseous	5 to 10 seconds
Solids	No limit
Pressure drop:	90% of height of fluidized bed (in H_2O)
Excess O_2:	30 to 50 percent
Air flow rate:	2.5 to 8.0 ft/sec
Typical bed thickness:	6 to 8 ft
Air pollution control	Acid scrubber, particulate scrubber, quench tower.
Startup and shutdown	Rapid startups and shutdowns possible. Continuous feed not necessary.
Bed particle size:	20 to 80 mesh

Source: Reference 20.

which are not practical for an FB system.[20] Pretreatment of wastes to reduce high moisture content is highly recommended for fluidized-bed incineration. Numerous standard dewatering techniques may be employed, including fractionation, filtration, and settling.

The consequences of a high concentration of fusable solid byproducts of waste combustion are very much the same for fluidized-bed incineration as those associated with the formation of inorganic salt eutectic mixtures described earlier. These materials may impair the fluidity of the bed by binding the granular solids into large, nonfluid solids.

10.3 HAZARDOUS WASTE INCINERATOR PERFORMANCE

The performance of various hazardous waste incineration systems has been the subject of extensive study. In almost all instances RCRA performance standards have been achieved despite the tremendous variability of waste characteristics and operating conditions employed. As noted by EPA in Reference 26, available data gathered by MITRE Corporation (Reference 27) demonstrate that all of the solvents of concern assessed in the 14 January 1986 proposed regulations have been, or are currently, destroyed through incineration technology. Detailed data on the composition of 413 waste streams incinerated at 204 facilities were obtained and analyzed by MITRE. It was concluded on the basis of this study that incineration is demonstrated technology for each of the solvent constituents listed under hazardous waste codes F001 through F005. These data, which show that 199-million gallons of solvent waste were incinerated yearly by the 204 facilities, are shown in Table 10.7. The following subsections will summarize performance data for each of the major incineration technologies. However, a summary of recent EPA sponsored facility testing activity is shown in Table 10.8.(6)

10.3.1 Liquid Injection Incinerator Performance Data

The results of numerous test programs have indicated that the liquid injection incinerator is a highly effective system for disposing of virtually all types of liquid hazardous wastes. Liquid injection incinerator data are

TABLE 10.7. SOLVENT CONSTITUENTS PRESENT IN INCINERATED WASTE STREAMS

Constituents	Number of waste streams containing constituent	Amount of constituent incinerated (million gallons)
Acetone	80	17.2
n-butyl alcohol	9	32.3
Carbon disulfide	3	0.128
Carbon tetrachloride	9	0.547
Chlorobenzene	21	6.18
Cresols	8	5.92
Cyclohexanone	4	0.344
1,2-dichlorobenzene	2	0.240
Ethyl acetate	24	9.62
Ethylbenzene	6	0.264
Ethyl ether	2	0.248
Isobutanol	9	4.50
Methanol	95	44.4
Methylene chloride	26	5.84
Methyl ethyl ketone	54	14.0
Methyl isobutyl ketone	10	4.68
Nitrobenzene	3	0.0057
Pyridine	9	4.38
Tetrachloroethylene	19	6.74
Toluene	103	17.3
1,1,1-trichloroethane	23	5.05
1,1,2-trichloro 1,2,2-trifluoroethane	2	0.0008
Trichloroethylene	15	3.69
Trichlorofluoromethane	2	0.401
Xylene	78	15.2
Total:		199

Source: MITRE Corporation. *Composition of Hazardous Waste Streams Currently Incinerated*. Prepared for U.S. EPA, Office of Solid Waste. 1983.

TABLE 10.8. INCINERATION FACILITIES TESTED

Facility	Control device	Waste	DRE[a] (number of nines)[b]	HCl control (average)	Average particulate emissions (g/dscf)
Commercial rotary kiln-liquid incinerator (87 million Btu/hr)	Packed-tower adsorber, ionizing wet scrubber	Drummed, aqueous, liquid organic waste with carbon tetrachloride, TCE[c], perchloroethylene, toluene, phenol	5.3	99.4%	0.67
Commercial fixed-hearth, two-stage incinerator (27 million Btu/hr)	Electrified gravel bed filter; packed-tower adsorber	Liquid organic and aqueous aqueous waste with chloroform, carbon tetrachloride, TCE, toluene, perchloroethylene	4.4	98.3%	0.178
Onsite two-stage liquid incinerator (6 million Btu/hr)	Packed-tower adsorber	Liquid organic waste with carbon tetrachloride, dichlorobenzene, TCE, chlorobenzene, chloromethane, aniline, phosgene	4.4	99.7%	0.027
Commercial fixed-hearth two-stage incinerator (2 million Btu/hr)	None	Liquid organic waste with TCE, carbon tetrachloride, toluene, chlorobenzene	4.7	<4 lb/hr[d]	0.089
Onsite liquid injection incinerator (4.8 million Btu/hr)	None	Liquid organic waste with analine, diphenylamine, mono- and dinitrobenzene	6.7	<4 lb/hr[d]	0.092

(continued)

TABLE 10.8. (Continued)

Facility	Control device	Waste	DRE[a] (number of nines)[b]	HCl control (average)	Average particulate emissions (g/dscf)
Commercial fixed-hearth two-stage incinerator ([illegible] million Btu/hr)	None	Aqueous and organic liquid waste with carbon tetrachloride, TCE, benzene, phenol, perchloroethylene, toluene, methylethyl ketone	4.8	4 lb/hr[d]	0.40
Onsite rotary kiln with liquid injection ([illegible] million Btu/hr)	Venturi scrubber with cyclone separators and packed-tower absorbers	Liquid organic, paint waste and filter cakes with methylene chloride, chloroform, benzyl chloride, hexachloroethane, toluene, TCE, carbon tetrachloride	5.3	99.9%	0.01
Commercial fixed-hearth two-stage incinerator ([illegible] million Btu/hr)	Venturi scrubber	Aqueous and organic liquids and solid waste with methylene chloride, chloroform, carbon tetrachloride, hexachlorocyclopentadiene, toluene, benzene, TCE	4.6	98.3%	0.075

[a] Destruction and removal efficiency (mass weighted average for all POHCs)

[b] For example, 99.995% DRE = 4.5 nines.

[c] TCE = trichloroethylene.

[d] No HCl control device; waste is low in total organic chlorine content.

available for a wide range of waste types. High performance levels were achieved based on the three primary measures of performance; i.e., DREs, particulate emissions, and HCl emissions.

The relationship between baseline levels of performance achievable by a liquid injection incinerator and key operating parameters such as combustion temperature, waste feed rate, and residence time, and key characteristics such as moisture content, ash content, and heat value, was studied extensively by Midwest Research Institute (1984). In this study, eight incinerators, equipped with liquid injection systems were tested. Some were exclusively liquid injection incinerators, whereas others were combination units including rotary kilns and fixed hearths.

While full details of process and waste characteristics are provided in Reference 28, it should be noted that all incinerators tested achieved the goal of greater than 99.99 percent destruction efficiency for liquid and solid wastes containing many solvents of concern, including chlorinated solvents.

The results of the MRI study and some key operating parameters are summarized in Table 10.9. The table also includes some data from another study (Reference 29) in which DREs were measured for a liquid injection incinerator at Plant I firing two industrial organic containing wastes. Again, additional details can be found in the original reference, and in other references such as 11, 21, 23, 25, and 30. Results of the extensive Reference 28 study are representative of the total body of incineration literature as it relates to the destruction of organics. These results are summarized below.

"1. Extensive analysis of organics emissions data provided the following insight into the factors affecting DRE:

- DREs for the incinerators tested were generally above 99.99 percent. The average DRE for volatile organic constituents was found to be 99.992 percent.

TABLE 10.9. SUMMARY OF RESULTS OF INCINERATOR TEST PROGRAMS

				Waste Characteristics			Average Incinerator Value				Performance		
Facility	No. of Runs	Average Waste Feed Rate (lb/hr)	Waste Constituents	Ash %	Chloride %	Moisture %	Temperature °C	Residence Time sec	Heat Input 10^6 Btu/hr	O_2, Stack %	DRE %	Particulate Emissions	HCl Emission Removal
Plant 1	[illegible]	Organic Waste [illegible]	Carbon Tetrachloride	[illegible]	8.96	90	1117-1154	4.5	66-87	10-	99.9961	151 mg/dscm	99.94%
			Trichloroethane								99.9976		
		Aqueous Waste [illegible]	Tetrachloroethylene	[illegible]	5.7	23				12.7	99.9985		
			Toluene								99.9985		
		[illegible]	Methylene Chloride	[illegible]	6.8	25					99.978		
			Methyl Ethyl Ketone								99.9994		
		[illegible]	1,1,2-Trichloroethane								99.9991		
			1,1,1-Trichloroethane								99.9998		
Plant 2	[illegible]	Organic Waste [illegible]	Chloroform	[illegible]	[illegible]	95	NA	NA	NA	NA	99.826	85% Removal	98.1%
			Carbon Tetrachloride								NA		
			Trichloroethylene	[illegible]	[illegible]	67					99.975		
		Aqueous Waste [illegible]	Tetrachloroethylene								99.9011		
			Toluene								99.9936		
			Phenol								99.981		
			Naphthalene								99.86		
			Diethyl phthalate								99.960		
			Butyl Benzyl Phthalate								99.9987		
Plant 3 [illegible]	[illegible]	[illegible]	Carbon Tetrachloride	[illegible]	21	60	1116	5.2	6.2	6.2	99.9838	136 mg/dscm	99.75%
			[illegible]								99.9917		
			[illegible]								99.934		
			[illegible]								99.99		
			[illegible]								99.920		
			[illegible]								99.997		
			[illegible]								99.9977		
			[illegible]								99.67		
			[illegible]								99.97		
			[illegible]								99.9999		
			[illegible]								99.948		
			[illegible]								99.997		
			[illegible]										
Plant 4 [illegible]	[illegible]	[illegible]	Methylene Chloride	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11.0	99.906	60 mg/dscm	NA
			Carbon Tetrachloride								99.9991		
			[illegible]								99.9982		
			Toluene								99.992		
			[illegible]								99.996		
Plant 5 [illegible]	[illegible]	[illegible]	Aniline	[illegible]	[illegible]	[illegible]	[illegible]	0.25	[illegible]	12.1	99.99999	167 mg/dscm	NA
			[illegible]								99.999		
			[illegible]								99.999		
			[illegible]								99.9999		
			[illegible]								99.99		

(continued)

TABLE 10.9. (Continued)

Facility	No. of Runs	Average Waste Feed Rate [illegible]	Waste Constituents	Waste Characteristics Ash %	Chloride %	Moisture %	Average Incinerator Value Temperature °C	Residence Time sec	Heat Input 10^6 Btu/hr	O_2, Stack %	Performance DRE %	Particulate Emission Removal	HCl Emission Removal
[illegible]	[illegible]	[illegible]	Carbon Tetrachloride Trichloroethylene Benzene Tetrachloroethylene Toluene Methyl Ethyl Ketone Phenol Naphthalene Butyl Benzyl Phthalate Bis(2EH)Phthalate	0.08 2.0	0.34 3.6	85 3.4	1050-1125	2.3	7.2	9.7	99.9995 99.9981 99.963 99.998 99.9938 99.9988 99.9996 99.98 99.99 99.995	NA	NA
[illegible]	[illegible]	[illegible]	Methylene Chloride Chloroform [illegible] Carbon Tetrachloride Trichloroethylene Tetrachloroethylene Toluene [illegible] Benzyl Chloride Hexachloroethane Naphthalene	0.10 27	25 39	2.5 15.2	1450	0.26	17	9.7	99.9992 99.9912 99.928 99.9999 99.9993 99.9994 99.9998 99.9999 99.9995 99.99 98	NA	99.89
[illegible]	[illegible]	[illegible]	Methylene Chloride Chloroform Methylene Bromide 1,1,1-Trichloroethane Carbon Tetrachloride Trichloroethylene Benzene Tetrachloroethylene Toluene Chlorobenzene Hexachlorocyclopentadiene Bis(2EH)Phthalate Chlordane Naphthalene Hexachlorobutadiene	5.6 0.05	2.5 0.02 2.5	3.3 85 3.6	966-1120	3.7	7.3	13.6	99.78 98.9 99.985 99.866 99.9986 99.9953 99.9868 99.9017 99.9947 99.857 99.99 99.95 99.999 99.996 99.98	NA	98.2
[illegible]	[illegible]	[illegible]	Total Organics[a]	—	8	—	1130-1415	0.16-0.19	5.2	7.2	99.999	NA	NA
	[illegible]	[illegible]	Hexachlorocyclopentadiene	—	75	—	1130-1070	0.17-0.18	7.4	6.6	99.99	NA	NA

NA = Not available

Source: References [illegible]

- DRE appears to be strongly correlated to concentration of the POHC in the waste feed. POHCs at higher waste feed concentrations were observed to be destroyed or removed to a higher degree. The phenomenon that caused this relationship was not identified.

- Analyses of data collected on this program showed no clear correlation between DRE and heat of combustion for POHCs.

- Data compiled from the eight tests were not sufficient to define parametric relationships between residence time, temperature, heat input, or O_2 concentrations and DRE.

- The data from the eight tests suggest that POHC levels in scrubber water and ash were generally very low or nondetectable. These data suggest that the majority of POHCs are destroyed rather than merely transferred to another media in the incineration process.

- Some Appendix VIII compounds detected in the stack (primarily trihalomethanes) appear to be stripped from the scrubber water by the hot stack gas. Trihalomethanes detected in the scrubber inlet water were not detected in the effluent water. The effect can be lower measured/calculated DREs even though the destruction mechanisms may not be affected.

2. Evaluation of organic emissions data for compounds classified as Products of Incomplete Combustion (PICs are defined in this program as Appendix VIII compounds detected in the stack, which were not found in the waste feed in concentrations above 100 ug/g) led to the following observations:

   - Stack gas concentrations of PICs were typically as high as or higher than those for POHC compounds in the stack.

- PIC output rate infrequently exceeded 0.01 percent of POHC input rate. (The 0.01 percent criterion was proposed in FR Vol. 45, No. 197, October 8, 1980.)

- The three likely mechanisms that explain the presence of most PICs are:

  a. Poor DREs for Appendix VIII compounds present at low concentration (<100 μg/g) in the waste feed;

  b. Input of Appendix VIII compounds to the system from sources other than waste feed (e.g., scrubber water); and

  c. Actual intermediate products of combustion reactions or products of complex side reactions including recombination.

- Data from the tests suggest that benzene, toluene, chloroform, tetrachloroethylene, and naphthalene have a high potential for appearing as byproducts of the combustion of organic wastes.

- A summary of the PICs detected in this study are given in Table 10.10.

3. Compliance with the particulate standard of 180 mg/Nm was not achieved at half of the sites tested. Particulate control devices were operated at five of the eight facilities, and two of these five failed to achieve the standard. Two of the three facilities without control devices also failed the particulate standard. Data from this study suggest that any facility firing wastes with ash content greater than 0.5 percent will need a particulate control device to meet the standard.

4. HCl emissions were generally easily controlled to meet one of the two criteria specified in the regulations - less than 1.8 kg HCl/hr or greater than 99 percent removal efficiency."

In addition to the effluent data discussed above, the study included analyses of two other residuals, ash and the scrubber liquor from the air pollution control device at four sites. The results of the analyses are shown in Table 10.11. The data indicate that both ash and scrubber liquor contain concentration levels that are below the proposed treatment levels for the solvents analyzed.

TABLE 10.10. PICs FOUND IN STACK EFFLUENTS

PIC	Number of sites	Concentrations (ng/L)
Benzene	6	12-670
Chloroform	5	1-1,330
Bromodichloromethane	4	3-32
Dibromochloromethane	4	1-12
Bromoform	3	0.2-24
Naphthalene	3	5-100
Chlorobenzene	3	1-10
Tetrachloroethylene	3	0.1-2.5
1,1,1-Trichloroethane	3	0.1-1.5
Hexachlorobenzene	2	0.5-7
Methylene chloride	2	2-27
o-Nitrophenol	2	25-50
Phenol	2	4-22
Toluene	2	2-75
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	18
2,4,6-Trichlorophenol	1	110
Bromomethane	1	1
Chloromethane	1	3
Pyrene	1	1
Fluoranthene	1	1
Dichlorobenzene	1	2-4
Trichlorobenzene	1	7
Methyl ethyl ketone	1	3
Diethyl phthalate	1	7
o-Chlorophenol	1	2-22
Pentachlorophenol	1	6
2,4-Dimethyl phenol	1	1-21

Source: Reference 28.

TABLE 10.11. RESIDUALS ANALYSIS AT FOUR FULL-SCALE INCINERATORS (mg/L)

	Site A		Site B		Site C		Site D	
	Ash Concentration[a]	Scrubber Liquor Concentration	Ash Concentration[a]	Scrubber Liquor Concentration	Ash Concentration[a]	Scrubber Liquor Concentration	Ash Concentration[a]	Scrubber Liquor Concentration
Carbon Tetrachloride	—	<0.010	<0.05-0.05	<0.001	<0.05	<0.001	—	<0.002
Chlorobenzene	—	—	—	—	<0.05	<0.001	—	0.001
Cresols	<4.05	<0.001	—	—	—	—	—	—
Methylene Chloride	—	<0.010	—	—	<0.05-0.08	b	—	—
Methyl Ethyl Ketone	—	<0.010	—	—	—	—	—	—
Tetrachloroethylene	—	<0.010	<0.05-0.1	<0.001	<0.05	<0.001	—	<0.001
Toluene	—	<0.010	0.2-0.7	<0.001-0.0026	0.24-1.8	b	—	<0.001-0.013
1,1,1-trichloroethane	—	<0.010	—	—	<0.05	<0.001	—	<0.001
Trichloroethylene	—	<0.010	<0.05-0.1	<0.001	<0.05	<0.001	—	<0.001

[a] Theoretical concentration if all of the constituents present in 100 grams of dry ash were completely extracted into 2 liters of solution.

[b] Concentration of compound in scrubber makeup water higher than concentrations in scrubber effluent.

Source: Reference 28.

10.3.2 Rotary Kiln Incinerator Performance Data

Rotary kiln incinerator performance in the destruction of hazardous wastes has been studied extensively. The results of such studies have indicated the effectiveness of rotary kiln systems for the destruction of solvent hazardous wastes.

The available performance data generally focuses on the destruction and removal efficiency achieved by the RK system relative to certain hazardous waste constituents ("the Principal Organic Hazardous Constituents", or POHCs). Also presented are the characteristics of wastes tested, including the heat content and moisture content of the waste feed, and the key operating parameters of the system during the test, including combustion temperature, residence time, and HCl and particulate matter removal efficiency. The results of three recent performance tests are summarized in Tables 10.12 through 10.14. In brief, the following results were common to these and other tests of rotary kiln incinerators.

- Destruction and removal efficiencies achieved by the rotary kiln generally exceeded 99.99 percent.
- A variety of wastes were handled without need for pretreatment.
- High combustion temperatures could be used.
- Long residence times were achievable.
- DREs were directly related to length of residence time, higher combustion temperatures, lowering of waste feed rate, and lower heat content.
- No correlation was found between DRE and certain waste constituent characteristics such as heat of combustion or autoignition temperature.

10.3.3 Fluidized-Bed Incinerator Performance Data

Fluidized-bed incinerators have proven to be an effective means of disposing of many types of hazardous wastes, as shown by a number of performance evaluation studies conducted by both industry and U.S. EPA. Several of the fluidized-bed systems in operation have become permitted

TABLE 10.12. PERFORMANCE TEST SYNOPSIS

Description of Program: Program conducted at Cincinnati Metropolitan Sewage District (MSD) hazardous waste incinerator, to verify U.S. EPA Trial Burn protocol and conduct environmental assessment.

Waste Form: Liquid hazardous wastes.

Constituents:

Compound	Range of DREs Reported
Chloroform	99.99
Carbon Tetrachloride	99.96 - 99.99
Tetrachloroethylene	99.97 - 99.99
Hexachloroethane	99.99
Trichloroethane	99.99
Tetrachloroethane	99.99
Dichlorobenzene	99.99
(several other non-solvent constituents were also noted)	

Number of Test Runs:

- 6 runs were conducted with a "Pesticide" waste containing chloroform, carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobenzene, and hexachlorocyclopentadiene.
- 3 runs were conducted with a "High Chlorine" waste containing trichloroethane, tetrachloroethane, bromodichloromethane, pentachloroethane, hexachloroethane, dichlorobenzene.

Effect of Varying Waste Feed Rate:

- Feed rate varied between 32.7 and 60.3 kg/min for "Pesticide" waste, and between 49.0 and 62.1 kg/min for "High Chlorine" waste.
- For pesticide waste, the average DREs went down as feed rate went up. The same effect was noted for the "high" chlorine waste.
- The HCl removal efficiency was also noted to decrease as feed rate was increased.

(continued)

TABLE 10.12 (continued)

Effect of Varying Residence Time:	• Range of residence time for pesticides was 1.7 - 3.7 secs and for high chlorine was 1.3 - 2.3 secs. • DREs were found to be directly related to residence time. As residence time went up, so did DRE. • HCl removal also went up as residence time went up.
Effect of Varying Temperature:	• A direct correlation between combustion temperature and DRE was noted for the first 3 pesticide runs, and the 3 high chlorine runs. As temperatures were increased, average DRE went up. No significant correlation was noted for the second 3 runs of pesticide waste. • Correlation between combustion temperature and HCl removal was difficult to assess. For pesticide runs, HCl removal increased with temperature. For the high chlorine runs, HCl removal decreased as temperature increased.

Source: Reference 31.

TABLE 10.13. PERFORMANCE TEST SYNOPSIS

Description of Program:	Test of Rotary Kiln to determine the effect on performance (measured by DRE) of varying certain waste and process characteristics.
Waste Form:	Liquid waste. Usual waste mixture combines liquid wastes (process effluents) and solid wastes (sludges, tars, etc.).
Waste Constituents:	Wastes with different chemical constituents were used inthe program. Included as constituents were the following solvent hazardous waste constituents: Acetonitrile (U003) Methyl Ethyl Ketone (U159) Ethylene Dichloride (U077) 1,4-Dioxane (U108) Toluene (U220) Methanol (U154) Chloroform (U044)
Process Characteristics	
Effect of Varying Bulk Gas Temperature:	Two bulk gas temperatures were used, 1600 and 1850°F. Two test runs were conducted. No significant correlation between bulk gas temperature and DRE was observed. DRE was greater than 99.99 at both temperatures (all test runs) for U077 and U220, while the average DRE for U159 and U108 was well below 99.99 at both temperatures.
Effect of Varying Kiln Temperature:	Two kiln temperatures were examined, 1300 and 1600°F. A strong direct correlation between temperature of the combustion zone and DRE was noted. DRE did not average above 99.99 at either temperature for either U003 or U154.
Effect of Varying Residence Time:	DRE was found to increase when residence time was increased from 1.2 secs to 3.3 secs. For U003, the increase was significant, but for U159, U108, U077, and U220, the increases was less pronounced.

(continued)

TABLE 10.13 (continued)

Waste Characteristics	
Autoignition Temperature:	No significant correlation between autoignition temperature and DRE was noted. Combustion was conducted at temperatures above the autoignition temperature of waste constituents.
Heat Content of Waste:	DREs were noted to increase when the heat content of the waste was increased from 6,000 Btu/lb to 10,000 Btu/lb. This is attributed to a higher flame temperature and more rapid evaporation of higher heat content waste mixtures.
Moisture Content of Waste:	DRE was noted to increase when moisture content was increased from 18% to 40%.
Heat of Combustion (of constituents):	No significant correlation was found between DRE and heats of combustion of waste constituents.
Solubility in Water:	An inverse correlation between solubility in water and DRE was noted. This is attributed to a higher rate of evaporation for those constituents which are less intermingled with water in solution.

Source: Reference 32.

TABLE 10.14. PERFORMANCE TEST SYNOPSIS

Description of Program: Trial Burn program conducted by the State of Michigan Department of Natural Resources.

Waste Form: Liquid wastes with solids.

Constituents:

Compound	Range of DREs Reported
1,1,1-Trichloroethane	99.996 - 99.998
Trichlorobenzene	99.992 - 99.995
Carbon Tetrachloride	99.996 - 99.999
2,4-Dichlorophenol	99.999
2,4,6-Trichlorophenol	99.999

Effect of Varying Waste Feed: DREs went down as waste feed rate was increased.

Effect of Varying Residence Time: DRE went up as residence time was increased.

Effect of Varying Temperature: DRE went up as temperature was increased.

Effect of Varying Excess Oxygen: DRE went up as excess O_2 went down.

Source: Reference 33.

hazardous waste units through demonstration of their ability to perform within guidelines established under RCRA. Trial burn data are available for several of these units in service which show that fluidized-bed incinerators are capable of destroying hazardous wastes of widely varying physical and chemical characteristics to levels exceeding a destruction and removal efficiency of 99.99 percent. The results have further indicated that the FB systems effectively control emissions of particulate matter and acid (HCl) produced during combustion of waste materials. The results also show that DREs are adversely affected, much as the other established incineration technologies are affected, by low concentration of POHCs in the waste, and by very high levels of moisture in the waste. The tests have also demonstrated the specific limitations of FB relative to sodium salt content, corrosivity, and fusable ash content, as discussed previously. A summary of typical performance results for a fluidized-bed incinerator is presented in Table 10.15.

The test program was conducted by plant officials under the supervision of U.S. EPA representatives who conducted independent sampling and analysis. The results of the test program were incorporated as part of a RCRA permit demonstration. During the test program, liquid hazardous waste containing five halogenated organic constituents (POHCs) and wastewater contaminated with the same organics were burned. The waste stream was generated by chemical manufacturing and consisted primarily of waste solvent. Analysis was made of destruction and removal efficiency (DRE), particulate emissions, and chlorine removal efficiency. Three test runs were made during the 2-day demonstration. In general, the results indicate that the fluidized-bed incinerator tested is capable of achieving performance levels which are within the guidelines established by the U.S. EPA for permitting. In summary:

- Three test runs were completed.
- The average waste feed rate was 610 lbs/hr and the average wastewater feed rate was 800 lbs/hr.
- The average heating value of the wastes was found to be 13,000 Btu/lb. The average heat input rate, therefore, was 8×10^6 Btu/hr.

TABLE 10.15. FLUIDIZED-BED INCINERATOR PERFORMANCE TEST RESULTS

Run No.	Waste Feed Rate (lbs/hr)	Waste Constituents (Principal Organic Hazardous Constituents)	Concentration in Waste Feed (% by weight)	Destruction and Removal Efficiency	Particulate Emissions (lbs/hr)	HCl Emissions (lbs/hr)
1	575.65	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.30	99.9918	8.95	0.40
		Trichloromonofluoromethane (TCMFM)	1.5	99.9906		
		Tetrachloroethylene	4.3	99.9976		
		Trichloroethylene	0.72	99.9965		
		1,1,1-Trichloroethane	5.3	99.9995		
2	632.55	1,1,2-Trichl-1,2,2-Trifl	0.29	99.9917	3.55	0.73
		TCMFM	1.2	99.9941		
		Tetrachloroethylene	3.8	99.9991		
		Trichloroethylene	0.68	99.9964		
		1,1,1-TCE	5.0	99.9996		
3	621.97	1,1,2-TC-1,2,2-TFE	0.28	99.9912	3.83	0.39
		TCMFM	1.9	99.9923		
		Tetrachloroethylene	3.6	99.9907		
		Trichloroethylene	0.89	99.9936		
		1,1,1-TCE	4.9	99.9994		

Source: Reference 34.

- Chloride content of the waste feed averaged 13.8 percent. Ash content of the waste averaged 4.7 percent.
- Combustion zone temperature averaged 2,201°F.
- DREs for the five POHCs averaged over 99.99 percent.
- Chloride removal efficiency averaged over 99 percent.
- Particulate emissions averaged 5.4 lbs/hr.
- PICs were not measured in the test.
- Scrubber water was found to contain methylene chloride, 1,1,1-trichloroethane, tetrachloroethylene, toluene, and ethylbenzene in very low amounts.
- Leachates were analyzed for heavy metals. None were detected in significant amounts.

10.3.4 Performance of Multiple Hearth and Fixed Hearth Furnaces

Although testing of multiple hearth and fixed hearth incinerators has been conducted, extensive performance data, other than that reported for two liquid injection/fixed hearth systems in Table 10.9, could not be obtained for this document. A potential source of data of this type may be from manufacturers of such systems, who operate pilot and test facilities to demonstrate the effectiveness of the performance of their systems for various wastes. Contact of manufacturers was made, but no data were available for this document from the sources contacted.

10.4 COSTS OF HAZARDOUS WASTE INCINERATION

The overall costs associated with the incineration of hazardous wastes are high relative to other hazardous waste treatment or disposal methods. Incineration facilities require large capital costs due to the size and complexity of the systems involved, and the requirements associated with the handling of hazardous wastes and their combustion products. Operating costs are high, primarily due to the large energy input required, and also as a consequence of large raw materials costs and stringent environmental control requirements. Incineration costs are difficult to specify, in general, because in each situation the number of factors impacting costs is large. These factors may be classified fundamentally as follows:

- Waste characteristics;
- Facility design characteristics; and
- Operational characteristics.

The general significance of many of the factors affecting incineration costs will be discussed in detail below.

Waste Characteristics-

As discussed in a previous section, all aspects of the incineration process design are related to waste characteristics. The chemical and physical properties of a waste considered for incineration govern the type of incinerator selected, the processing capacity, environmental controls employed, pretreatment employed, required maintenance and equipment lifespan, and operational parameter levels. Several waste characteristics which significantly affect the costs of incineration are described below:

- Physical State--Physical state dictates the type of incinerator and the type of waste feed mechanism selected. Liquid injection incinerators, for example, are applicable only to liquid wastes, Limited data available on prices charged by commercial incinerators suggest that solid and sludge wastes are more expensive to incinerate than liquid wastes.
- Heat Value--Heat value is used as a measure of auxiliary fuel requirement. The higher the heat value of a waste, the less fuel is required to sustain combustion.
- Rheological Characteristics--The way in which liquid viscosity of a waste changes with temperature is important in determining the need for preheating, waste feed mechanism, and incinerator type. Some of the wastes are easily handled at higher temperatures, while others maintain viscosities which render then nonpumpable and/or nonatomizable over practical limits of temperature.

- Water Content--Water content of a waste strongly affects temperature and destruction efficiency of the combustion system. In some cases, dewatering of wastes is conducted as a pretreatment operation.

- Chloride Content--The chloride content of a waste has strong bearing on the air pollution control methods employed at an incinerator. High levels of chlorine necessitate acid gas scrubbing and also require combustion methods which prevent the formation of toxic chlorine gas.

- Ash Content/Heavy Metals Content--The amount of ash which will be formed in combustion, and the nature of the ash is related to the inorganic salt and heavy metal content of a waste to be incinerated, and greatly affects the particulate matter air pollution control requirement and the ash collection and disposal system design.

The impact of various waste characteristics on incineration costs may, in some cases, be measured directly. A survey was conducted of a cross-section of hazardous waste incineration facilities operating commercially in the United States, and it revealed that pricing structures are often established based on certain waste characteristics.[17,18,19,35-38] As shown in Table 10.16, chloride content and ash content commonly are used to establish surcharges based on additional air pollution control requirements. The physical form of the waste may also be seen as leading to price differentials. In general, solid and sludge wastes cost more to incinerate than liquid wastes.

Facility Characteristics--

Facility characteristics; i.e., the design and size of incineration unit equipment, are measured in terms of capital costs. Capital costs for incineration facilities are high relative to many other hazardous waste management technologies, which are generally less complex and sensitive to thermal and mechanical tolerances. For each incineration technology, there is a large variation in the designs available commercially, and great differences in the pricing policies of manufacturers. As a result, it is difficult to specify a range of costs for any particular type of system.

TABLE 10.16. SURVEY OF HAZARDOUS WASTE INCINERATORS - COSTS OF INCINERATION AND COST IMPACTING FACTORS

Facility	Incineration System	Costs to Incinerate Hazardous Wastes		Additional Costs	
		Type of Waste	Cost ($)	Basis	Cost ($)
A	Liquid Injection/ Rotary Kiln	Blendable[a] aqueous	0.18/lb	Phase separation	0.3475/lb
		Blendable organic	0.2675/lb		
		Directly-burned aqueous	0.2050/lb		
		Directly-burned organic	0.2850/lb		
		Directly-burned sludges or solids	0.5/lb		
B	Liquid Injection/ Rotary Kiln	Liquids	39/55 gal. drum	Chloride content or ash content	N/A
		Solids and sludges	125/55 gal. drum		
C	Liquid Injection/ Rotary Kiln	Any	0.25/lb	Chloride content or ash content	0.002/lb per each 1% of chloride or ash content
D	Liquid Injection	Liquids	0.86/gallon	Suspended solids	0.01/gal per 1% content
				Metals (e.g. chromium)	0.0005/100 ppm/gallon
				Chlorine	0.02/gal per 1% chlorine
E	Liquid Injection/ Rotary Kiln	Bulk liquids	1.93/gallon	Handling fee	25/drum
		Drummed liquids	230/drum	"Approval" charge	150/job
		Drummed solids	300/drum		

[a] Blendable defined as possessing a viscosity of below 10,000 SSU.

Source: References 17, 18, 20, 19, 35-38.

To determine the cost of a hazardous waste incineration facility, several key factors must be assessed. The elements contributing to the capital cost of a "typical" incineration facility are presented in Table 10.17. Several of the key factors influencing capital cost are listed below:

- Size requirments - flow rates, heat input capacities, exhaust rates, etc.;
- Equipment lifespan;
- Pretreatment requirements;
- Heat recovery;
- Environmental control requirements;
- Feed mechanisms; and
- Equipment availability.

The size requirements of the system have the most bearing on capital costs, while the environmental control equipment costs may be the largest element of the overall capital costs. The capital costs of a particular hazardous waste incineration system are strongly affected by the overall availability of that technology. Certain systems, such as liquid injection incinerators, are manufactured by many companies. Other technologies, most notably the newer type systems, are manufactured by a few, or in many cases, only one company.

Capital cost data available for hazardous waste incineration systems were limited. Several manufacturers of incineration systems were contacted, but most were reluctant to specify costs for their systems because the cost for a specific application is dependent upon so many different factors. A study conducted by McCormick, et al.,[5] provided cost estimation curves for several of the established hazardous waste incineration technologies: liquid injection, rotary kilns, and hearth incinerators. These cost curves, including estimation curves for heat recovery systems (waste heat boiler) and acid gas scrubbing systems, are presented in Figures 10.5 through 10.10. This

TABLE 10.17. ELEMENTS OF CAPITAL COST FOR INCINERATION SYSTEMS

I. Incineration System
  A. Waste conveyance
    1. Open or compaction vehicles, commercial containers
    2. Special design containers
    3. Piping, ducting, conveyors
  B. Waste storage and handling at incinerator
    1. Waste receipt and weighing
    2. Pit and crane, floor dump and front-end loader
    3. Holding tanks, pumps, piping
  C. Incinerator
    1. Outer shell
    2. Refractory
    3. Incinerator internals (grates, catalyst)
    4. Burners
    5. Fans and ducting (forced and induced draft)
    6. Flue gas conditioning (water systems, boiler systems)
    7. Air pollution control
    8. Stacks
    9. Residue handling
    10. Automatic control and indicating instrumentation
    11. Worker sanitary, locker, and office space

(continued)

TABLE 10.17 (continued)

II. Auxiliary systems

   A. Buildings, roadways, parking areas

   B. Special maintenance facilities

   C. Steam, electrical, water fuel, and compressed air supply

   D. Secondary pollution control

      1. Residue disposal 9landfill, etc.)

      2. Scrubber wastewater treatment

III. Nonequipment expenses

   A. Engineering fees

   B. Land costs

   C. Permits

   D. Interest during construction

   E. Spare parts inventory (working capital)

   F. Investments in operator training

   G. Start-up expenses

   H. Technology fees to engineers, vendors

Source: Reference 16b.

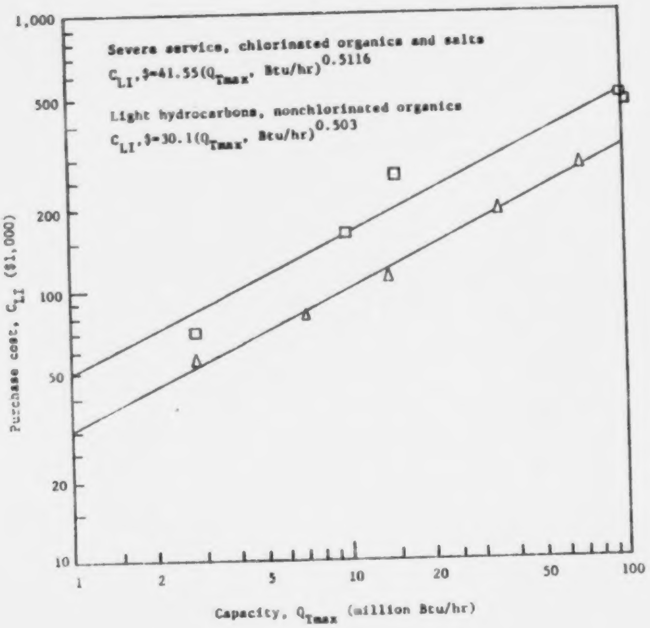

Figure 10.5. Purchase cost of liquid injection system (May 1982).

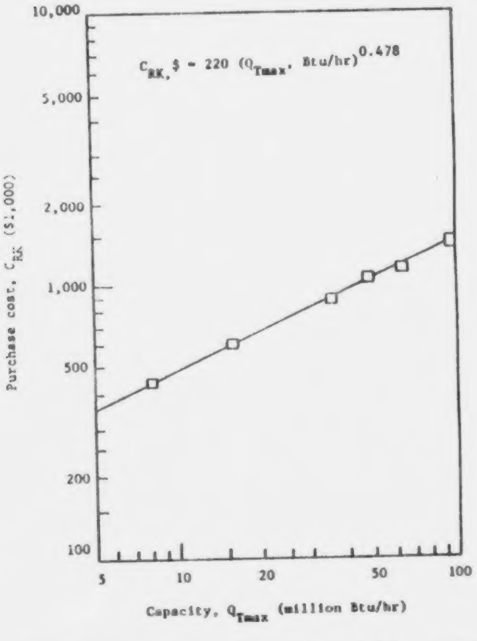

Figure 10.6. Purchase cost of rotary kiln system (May 1982).

Source: Reference 5

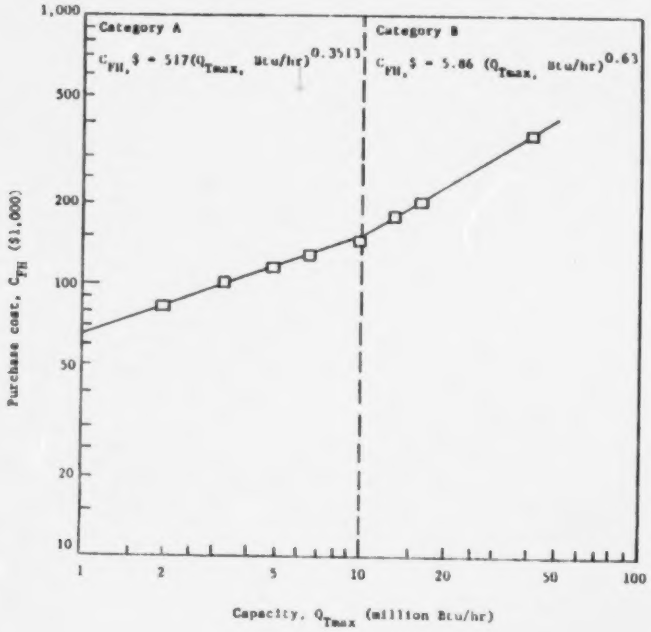

Figure 10.7. Purchase cost of hearth incinerators (mid 1982).

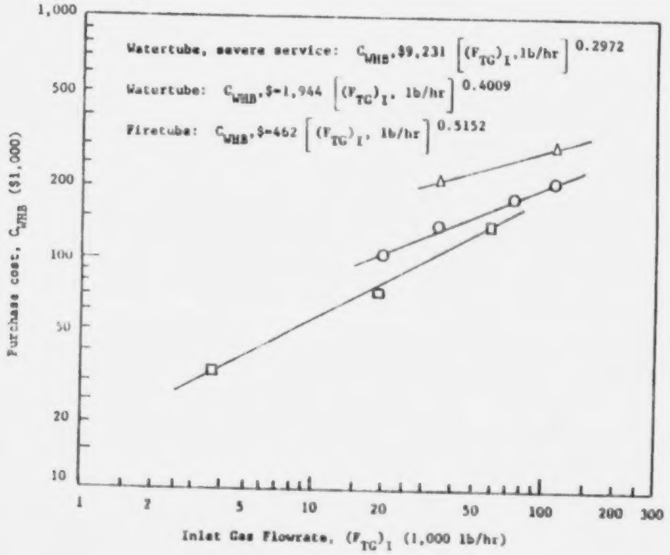

Figure 10.8. Purchase cost of waste heat boilers (July 1982).

Source: Reference 5

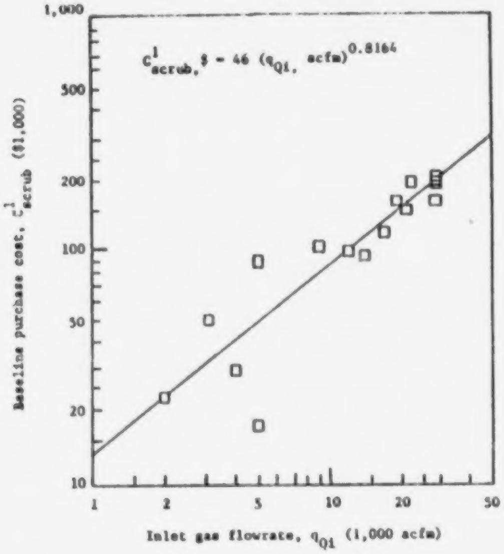

Figure 10.9. Purchase cost of scrubbing systems receiving 500 to 550°F gas (July 1982).

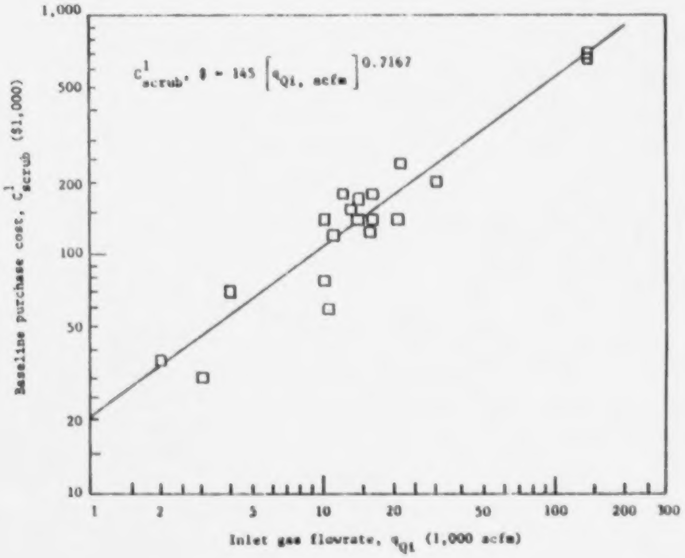

Figure 10.10. Purchase costs for typical hazardous waste incinerator scrubbing systems receiving 1800 to 2200°F gas (July 1982).

Source: Reference 5

information was generated in 1982, and has been updated to reflect the changes in the Chemical Engineering Plant Index between May 1986 and the date for which costs were estimated in Reference 5. A study conducted by MITRE Corporation in 1981 in which several visits were made to incinerator manufacturers generated additional cost data summarized in Table 10.18.

In general, it may be noted that certain hazardous waste technologies are considered to be more expensive in terms of capital costs than are others. Rotary kilns are most expensive. Relative capital costs for the five established incineration technologies are as follows in order of decreasing cost:

Rotary Kiln

Fluidized-Bed

Multiple Hearth

Liquid Injection

Fixed Hearth

Operating Characteristics--

Numerous factors impact the operating costs of a hazardous waste incineration facility. The most significant factor governing operating costs is energy usage. Energy is used in incineration to heat wastes in combustion, and to operate materials transport and control systems. In many cases, the energy usage of an incineration system is large enough to justify the costs of installing and operating heat recovery systems. A summary of the more important operating characteristics, besides energy usage, affecting the costs associated with incineration is presented below:

- Residence Time--Residence time affects the volume of the combustion chamber, secondary combustion requirement, and the exhaust rate. Residence time may be increased by employing devices such as baffles or recirculation blowers.

- Temperature--Temperature affects the volume and type of the incinerator refractory lining, volume of insulation for other systems, and the need for heating and cooling systems.

TABLE 10.18. SUMMARY OF COST DATA COMPILED BY MITRE CORPORATION, 1981

Facility	Incineration Technology	Capacity (mmBtu/hr)	Capital Cost ($)	Description of Cost Factors
1	Fluidized Bed	10	700,000	Without energy recovery. Scale-up factor for cost estimation is 0.6 exponent.
2	"Packaged" Rotary Kiln	---	40-50,000/(100 lbs/hr)	Installed cost, including heat recovery and air pollution control.
3	Rotary Kiln	37.5	800,000	Not installed. Includes 1 item of air pollution control. Estimated installation cost was 20 percent.
4	Rotary Kiln	80-150	10-15 x 10^6	Total installed cost.
		0.5	600,000	Total installed.
		1.02	1.9 - 2.2 x 10^6	All not installed.
		1.24	2.34 - 2.66 x 10^6	
		14.1	2.66 - 3.04 x 10^6	
		17.0	3.25 - 3.65 x 10^6	
5	Rotary Kiln	90	8.5 x 10^6	Total installed.

(continued)

TABLE 10.18. (continued)

Facility	Incineration Technology	Capacity (mmBtu/hr)	Capital Cost ($)	Description of Cost Factors
6	Liquid Injection	5	150,000	o Base cost, not installed, no APC, heat recovery.
			300,000	o Total installed with APC.
7	Fixed Hearth	5	150,000	o Base cost, no APC or heat recovery, not installed.
			300,000	o Installed with APC.
8	Liquid Injection	18	500,000	o Not installed.
		70	1.5×10^6	o Total installed cost.
				o Scale-up factor is exponent - 0.65.
9	Combined Liquid Injection and Rotary Kiln	150	2.2×10^6	o Not installed. No APC, heat recovery.
				o Estimated cost of APC given is 1.2×10^6.
10	Liquid Injection	30	400-500,000	o With boiler and scrubber, not installed.
11	Pyrolysis	3,000 lbs/hr	1×10^6	o Including heat recovery, no APC installed.
		6,000 lbs/hr	4×10^6	

Source Reference 20.

- Raw Materials Usage--A variety of raw materials are used in incineration systems, including chemical agents, fluidized-bed granular material, scrubber and cooling tower water, sorbents, and oxygen. The consumption of these materials leads to additional cost considerations.

- Maintenance--Maintenance requirements for incineration systems is considered high due to the number of systems involved and the thermal and mechanical stresses they operate under. The maintenance of refractory linings is considered a particularly significant cost consideration.

- Disposal--Disposal of solid and liquid combustion byproducts can be a very expensive proposition depending on the characteristics of the materials produced. In some cases, systems are limited in applicability based on disposal costs of, for example, heavy metals containing wastes.

Because of the uncertainties in many of the above items, it is difficult to assign meaningful values to elements of operational costs. These factors, however, have been considered by operators in assigning differential values based on waste characteristics (see Table 10.16).

10.5 STATUS OF DEVELOPMENT

10.5.1 Hazardous Waste Incinerator Manufacturing Industry[19,20]

Several surveys have been conducted to determine the number of companies currently involved in the development, manufacture, and installation of hazardous waste incineration systems. Investigation of the current hazardous waste incinerator market in 1982, indicates that there are approximately 67 companies known to be actually involved. This number may not necessarily include the number of companies who are devloping newer, more innovative thermal technologies. The conventional technologies offered by these commercial companies are summarized in Table 10.19. In general, the following conclusions, drawn by the MITRE corporation in 1982, are supported by these data:

- "About 342 incinerators have been put into hazardous waste services since January 1969. These units were manufactured by 29 companies, all of which were based in the United States at the time the units

TABLE 10.19. NUMBER OF HAZARDOUS WASTE INCINERATORS IN SERVICE IN THE U.S.A.

Type	No. of Companies Offering	No. in H.W. Service	Range of Capacities	Numerical Share of Market (%)
Liquid Injection	23	219-231	3-300 mmBtu/hr	64
Rotary Kiln	17	42	1-150 mmBtu/hr	12.3
Fixed Hearth[a]	15	64	200-2500 lbs/hr	18.5
Multiple Hearth	2	7	1000-1500 lbs/hr	2.0
Fluidized Bed	9	9	N/A	2.6

[a] Includes other hearth-type systems including Pulse Hearth (2), Rotary Hearth (2), Reciprocating Grate (1).

N/A - Information not available.

Source: Mitre, 1982 (Reference 20).

U.S. EPA, 1985 (Reference 19).

were delivered. Within the past year one of these companies (BSP Envirotech) was purchased by a West German firm, the Lurgi Corporation. The count of 342 units is believed to be reasonably accurate, but cannot be exact for the following reasons:

  - A number of small vendor companies have disappeared since 1969. These companies have probably manufactured a few incinerators which are still in use, but their existence could not be determined.
  - Incinerators originally sold for hazardous waste disposal, or for nonhazardous wastes, could be operating, at least part time, on the other waste.
  - Some incinerators have been manufactured strictly in accordance with a customer's specifications and the manufacturing company has no knowledge of, or declines to speculate on, the nature of the purchaser's wastes.
  - A few incinerators which have been manufactured since January 1969 are probably no longer in use. A vendor will not generally know this.
  - A few incinerators manufactured since 1969 cannot fulfill the design function and are not operating. Vendors will not voluntarily acknowledge these.

- The most common type of hazardous waste incinerator is liquid injection, representing 64.0 percent of all hazardous waste incinerators in service. This type of incinerator is not designed to operate on liquids containing any significant amount of salts or other suspended or dissolved solids,
- The next most common types of hazardous waste incinerators are the fixed hearth (FH) and the rotary kiln (RK), with 17.3 and 12.3 percent, respectively, of the total manufactured. Both of these types of units will dispose of solid and/or liquid wastes, plus fumes.
- Although there are nine companies offering fluidized-bed (FB) incinerators, only nine such units are in hazardous waste sevice. Apparently most of these nine companies belive that the market is potentially good for this technology.
- Two companies are actively marketing fused salt bath technology, but there are no units in service or under construction yet.

- Of about 219 liquid injection units in service, about 129 (59 percent) were produced by two companies, John Zink and Trane Thermal. The data furnished by Zink are not well verified. Of 23 companies marketing LI incinerators, eight have sold no units to date. However, several of the eight indicate that sales are imminent.

- Of the 17 companies offering rotary kiln incinerators, eight have sold none to date.

- Of the nine companies offering fluidized-bed incinerators, five have sold none to date.

- Of a total of 57 companies offering 14 types of incinerators, 28 have sold no units in the United States (Several companies represent European technology, and all have sold at least one unit, each, in Europe).

- The fact that 28 (of the total of 57 companies) have not sold any units to date is indicative of the extent of: (1) new technology being made available in the United States by both U.S. and foreign companies; (2) the formation of new corporate ventures in the field of technology; and (3) efforts by European companies to invade the U.S. market. It is therefore believed that the market, or technology, is not static at this point in time.

- Two companies are allegedly developing new technology, which they would not describe at this time. It is known that other companies are researching other techniques for hazardous waste incineration, but these technoques are not described in this report. The new processes included plasma, microwave plasma, and several unusual fluidized-bed techniques."[20]

10.5.2 Liquid Injection Incineration

Liquid injection incinerators are currently the most common type of hazardous waste incinerator in service in the United States. In 1982, MITRE estimated that 219 of these units were in service representing 64.0 percent of the total. The number of companies reported to produce such units for hazardous waste service was 23. Many manufacturers of liquid injection and other types of incinerators can be found listed in McGraw-Hill's Chemical Engineering Equipment Buyers' Guide. No major breakthroughs in liquid injection technology are anticipated.

Although considerable work has been performed to demonstrate the benefits of cyclonic systems as opposed to conventional systems, due in part to increased turbulence (and therefore, better mixing of waste and air), it is questionable as to what impact such designs will have on the LI market. According to manufacturers, many customers are seeking the simplest system possible, to minimize maintenance problems. Manufacturers of liquid injection systems feel that costs will remain low and possibly improve relative to other incineration techniques.[13,24] Liquid injection incineration is probably the lowest cost incineration alternative due primarily to the simplicity of the design and lack of moving parts requiring large amounts of energy.

The advantages and limitations of liquid injection incineration can be summarized as follows.

Advantages--

1. Liquid injection incinerators are the most cost effective means of incinerating atomizable liquid hazardou wastes. Performance tests indicate DREs of over 99.99 percent have been achieved for most types of liquid wastes.
2. Capable of incinerating liquid wastes containing a wide range of physical and chemical properties.
3. Continuous removal of ash may not be required.
4. Capable of operating with no particulate control system, except for moderate to high ash content wastes.
5. High temperature combustion of up to and exceeding 3,000°F is possible.
6. Capable of high turndown ratio (maximum-to-minimum feed rate) which provides flexibility in feed requirements.
7. Fast temperature response to changes in fuel flow rate.
8. Simple, adaptable design. Can retrofit a liquid injection system to an existing incineration system.
9. Virtually no moving parts. Generally low maintenance requirements and low maintenance costs.
10. Overall low capital and operating costs.
11. Most widespread application of any incineration technology. Proven in many applications. Has achieved RCRA permit status.

Limitations--

1. Capable of incinerating only liquid wastes that can be atomized through a burner nozzle.
2. Nozzles are a source of plugging, erosion, and corrosion.
3. Difficult to incinerate high surface tension liquids.
4. Difficult to control carry-over of unbound liquid droplets.
5. Can experience mixing problems, leading to inefficient combustion.
6. Can experience high emissions of oxides of sulfur and nitrogen, acid gases, particularly during high temperature operation.
7. May not destroy waste constituents effectively at low concentrations.

10.5.3 Rotary Kiln Incinerators

Rotary kiln incinerators have gained widespread commercial acceptance in the hazardous waste management industry, despite being one of the more costly available alternatives. This acceptance is due primarily to the versatility of rotary kilns. There are many facilities, for example, which currently employ a rotary kiln as their sole means of disposing of both hazardous and nonhazardous wastes. In general, it is believed that as more emphasis is placed on utilizing available alternatives to land disposal of hazardous wastes, "multipurpose" technologies such as rotary kiln incinerators will gain more acceptance. In addition, the utilization of rotary kiln technology may increase significantly if high temperature industrial kiln processes are utilized as a means of hazardous waste disposal. Among those technologies currently being studied are cement and lime rotary kiln systems. A great reduction in cost may be realized by using existing industrial systems for hazardous waste disposal.

As indicated in Table 10.19, 17 companies were identified in 1982 as having developed, and are now actively marketing rotary kiln incinerators specifically for hazardous waste disposal. Of that number, at least nine companies have sold units which are currently in service at hazardous waste management facilities.[19] In addition to these companies, there are numerous other firms who have developed and produced rotary kiln systems for industrial applications such as aggregate and lime rotary kilns. As the industrial processes are developed and put into use for hazardous waste disposal, many of these firms may become more involved in marketing their systems for hazardous waste disposal.

The advantages and disadvantages of rotary kiln incinerators are as follows:

Advantages--

1. Will incinerate a wide variety of liquids, slurries, sludges, tars, or solid wastes, either separately or in combination.
2. Adaptable to a wide variety of feed mechanism designs, including those for containerized wastes.
3. Characterized by high turbulence, thus provides good mixing of waste with combustion air, and good dispersion of waste to increase heat transfer surface area.
4. Can operate at temperatures up to or exceeding 2,500°F.
5. Can control residence time by adjusting rotational speed. Thus, slow burning materials may be retained for a very long period of time.
6. Can achieve a turndown ratio (maximum to minimum feed rate) of approximately 2:1.
7. There are no moving parts within the kiln.
8. Continuous ash removal does not interfere with oxidation of wastes.
9. Requires minimal preparation of wastes.
10. Adaptable for use with wet gas scrubbing system.

Limitations--

1. High capital costs for installed system, particularly if secondary combustion and heat recovery are included.

2. Maintenance costs are high due to refractory lining maintenance and replacement, and repair and maintenance of various rotating parts.

3. High energy costs required due to relatively low thermal efficiency.

4. Limited use for highly corrosive materials which could potentially damage refractory lining.

5. Air inleakage from end seals is a common operational problem.

6. Some fusable material may collect in kiln.

7. May generate high levels of airborne particulates due to increase turbulence. Requires additional control for particulate matter.

10.5.4 Fuidized-Bed Incinerators

Fluidized-bed incineration is a processing technology that is finding increasing commercial application at facilities for the purpose of managing hazardous wastes. Standard fluidized-bed systems are an established technology alternative, actively produced and marketed by about ten companies. It is expected that their relatively small current market share of approximately 3 percent (as determined by MITRE in 1982), will rise, perhaps surpassing less efficient systems such as multiple hearth furnaces. However, due to the fact that their applicability to wastes with widely varying physical and chemical characteristics may never approach that of rotary kilns, or that their operating costs for liquid wastes may never be competitive with liquid injection systems, fluidized-bed incinerators may never become a predominant technology for the incineration of hazardous wastes.

Of the ten fluidized-bed incinerators known to be in service burning hazardous wastes, the majority, seven, were sold by one firm. The company has sold most of these units to petroleum refineries, where they are in operation disposing primarily of sludges and a limited amount of contaminated sand and soil and off-specification liquid solvent wastes. Only one FB system was dedicated in 1982 solely to the destruction of hazardous wastes.[20]

The advantages and disadvantages of fluidized-bed incineration have been summarized in Reference 9, as noted.

> "Advantages associated with fluidized-bed incineration include the following:
>
> 1. General applicability for the disposal of combustible solids, liquids and gaseous wastes.
> 2. Simple design concept, requiring no moving parts in the combustion zone.
> 3. Compact design due to high heating rate per unit volume (100,000 to 200,000 Btu/hr-ft^3 (900,000 to 1,800,000 kg-cal/hr-m^3)) which results in relatively low capital costs.
> 4. Relatively low gas temperatures and excess air requirement which tend to minimize nitrogen oxide formation and contribute to smaller, lower cost emission control systems.
> 5. Long incinerator life and low maintenance costs.
> 6. Large active surface area resulting from fluidizing action enhances the combustion efficiency.
> 7. Fluctuation in the feed rate and composition are easily tolerated due to the large quantities of heat stored in the bed.
> 8. Provides for rapid drying of high moisture content materials, and combustion can take place in the bed.
> 9. Proper bed material selection suppresses acid gas formation; hence, reduced emission control requirements.
> 10. Provides considerable flexibility for shock load of waste; i.e., large quantities of waste being added to the bed at a single time.
>
> Potential disadvantages include:
>
> 1. Difficult to remove residual materials from the bed.
> 2. Requires fluid bed preparation and maintenance.
> 3. Feed selection must avoid bed degradation caused by corrosion or reactions with the bed material.

4. May require special operating procedures to avoid bed damage.
5. Operating costs are relatively high, particularly power costs.
6. Possible operating difficulties with materials high in moisture content.
7. Formation of low melting point eutectics is a serious problem.
8. Hazardous waste incineration practices have not been fully developed.
9. Not well suited for irregular, bulky wastes, tarry solids, or wastes with a fusible ash content.

There are two sources of waste incineration inefficiency associated with fluidized-bed incineration: (1) incomplete oxidation of the volatiles and (2) loss of solids which contain unoxidized combustibles. The incomplete oxidation of solids presents the greater difficulty in attaining complete incineration because solids generally require a longer time for complete oxidation than gases at a specific temperature. The loss of incompletely oxidized solids can occur by elutriation or by removal with the bed material. The bed material must be removed and regenerated, continuously or periodically, because of build up of noncombustibles or attrition of the inert heat carrier. Inadequate residence time of solid wastes is a major cause of inefficiency of fluidized-bed incineration."[9]

10.5.5 Environmental Impacts of Incineration

Incineration processes potentially affect the environment through generation of air emissions, and liquid, sludge, and solid wastes. As a result, EPA has established environmental standards of performance for incinerators in the RCRA permit process. Most incinerators must be equipped with appropriate air pollution control systems, leading to higher capital and operating costs. Environmental impacts associated with incineration are, therefore, a significant factor in the determination of the appropriateness of incineration as a management option for hazardous wastes.

10.5.5.1 Air Emissions--

Air emissions of pollutants produced in incineration are a primary area of environmental concern. Emissions may be emitted from the incinerator stack and from fugitive emission sources. Emissions from incinerators primarily consist of the following "criteria" pollutants: oxides of nitrogen and sulfur, and particulate matter. Other air pollutants of concern include undestroyed organics such as benzene, toxic heavy metals (in particles), hydrochloric acid, and other acid gases.

As part of the RCRA permit process, incinerators must demostrate their ability to achieve various performance levels established by EPA. Among the performance criteria are emission standards for hydrochloric acid gas and particulate matter. These standards are:

1. Hydrochloric acid emissions are limited to a rate of 4 lbs/hr or, if acid gas scrubbing is employed, a scrubbing efficiency of 99 percent or greater; and
2. Particulate matter emissions are limited to 0.08 grains per dry standard cubic feet of flue gas at 7 percent oxygen (180 milligrams per dry standard cubic meter).

Emissions from incinerators are also regulated under Federal NESHAPs and state air toxics program standards. These may affect, in particular, the emissions of heavy metals such as lead or mercury vapors.

Available technologies for the control of emissions from hazardous waste incinerators includes devices to control emissions of particulate matter, acid gases, oxides of sulfur, and possibly oxides of nitrogen. Gaseous pollutant control devices include various wet and dry scrubbers. Both wet and dry scrubbing systems are effective in removing acid gases, although the dry scrubbing systems are newer and, as a result, not as well established as the wet systems. Oxides of nitrogen emissions can sometimes be minimized by the use of combustion modifications which reduce the peak flame temperature in an incinerator.

For control of particulate matter, the primary candidates are the wet and dry electrostatic precipitators (ESPs), ionizing wet scrubbers, and baghouses. Conventional scrubbers are not very effective in the removal of fine particulate matter. Particulate matter control devices must be compatible with the acid removal device. A wet acid scrubber is more compatible with a wet ESP or the ionizing wet scrubber than with a baghouse.

Since baghouses are compatible only with a dry gas system, the use of baghouses on hazardous waste incinerators is not as prevalent as ESP usage. Properly designed baghouses and ESPs are both effective particulate matter control devices. Discussion of the various types of emission control devices used on hazardous waste incinerators and their control efficiency capabilities can be found in numerous texts and publications dealing with air pollution control and incineration.

10.5.5.2 Liquid and Solid Wastes Generation--

Wastes formed both in the combustion unit and in pretreatment and air pollution control systems constitute a potential environmental hazard which must be properly managed. Presence of hazardous materials in the incinerator ash, scrubbing liquor, and scrubber sludges is primarily dependent upon two factors: composition of wastes fed; and destruction effectiveness of the incinerator. The primary constituents of concern in these residues are thermally inert materials such as toxic heavy metals. Toxic organic compounds are generally not a significant contaminant of these streams, owing to good destruction efficiencies.

Ash from incineration--Incinerator ash formed during the combustion reaction consists almost entirely of thermally inert materials (metals and other inorganics) introduced in the waste feed. Ash, not emitted with the combustion flue gas, generally collects at the bottom of the incinerator unit. Many incinerator designs include a conveyor system which continuously removes ash from the bottom of the unit for subsequent disposal. Contaminated ash is now commonly disposed of in a Class I landfill. As noted in Reference 28, ash residuals from incineration have been found to be suitable for landfill disposal. Alternatives to direct landfilling, if required, could include encapsulation/solidification treatments.

Scrubber Liquor/Scrubber Sludges--Scrubber systems, which directly contact the gaseous by-products of combustion with liquid (or solid) media, most commonly water, may produce contaminated liquid or solid waste streams.

The primary contaminants of such streams are toxic solid particles carried as fly ash, acids such as hydrochloric acid formed in combustion, and various organic products of incomplete combustion. The quantity, quality, and types of liquid wastes formed from the control equipment is dependent on the constituents of the waste feed, destruction efficiency, and collection efficiency.

Liquid effluents from scrubber and quench systems usually will undergo neutralization and removal of solids before they are discharged to local sewage systems. A very common practice is to discharge these streams to settling ponds (volatilization of organics from these ponds is not considered a significant problem). Sludges are commonly treated in a sewage sludge incinerator, or are dewatered and directly landfilled. Residual analysis of scrubber liquor and sludges[28] have indicated that they are essentially free of organic materials.

10.5.6 Summary--

The advantages and disadvantages of the various incineration technologies available for the destruction of solvent hazardous wastes are presented in Table 10.20. In general, most of the common incineration technologies might be used to burn solvents, depending upon the individual characteristics of the waste.

TABLE 10.20. SUMMARY OF INCINERATION TECHNOLOGIES

Incineration Method	Limitations	Advantages	Disadvantages	Approximate Costs	
				Capital	Operating
Liquid Injection	Feedstock must be atomizable; relatively free of particulates	Can process all types of hazardous liquids	Requires pretreatment to remove impurities, heat, and blend	$4-500,000 for 30 mmBtu/hr (installed, with heat recovery and APC 1982)	$1-250/1000 gal
Rotary Kiln	Requires large batch throughput to be practical or economical	Can process virtually any type of waste; can coincinerate various types of wastes	Requires air pollution controls	$40,000-50,000/(100 #/hr) $10-15 x 10^6 for 80-150 mmBtu (total installed, 1982)	$2500-1000/ton/day
Fluidized Bed	Requires large batch throughput; limited to liquids or non bulky solids; no sodium salt wastes	Can process many wastes types; good temperature response in processing	Requires periodic bed replacement; requires air pollution controls	$700,000 for 10 mmBtu (total installed, no heat recovery, 1982)	N/A
Fixed Hearth	Requires afterburner; can't burn liquids if use continuous ash recovery	Can achieve very high combustion temperatures; low maintenance required	Not energy-efficient; requires higher temperatures and residence times	$3-400,000 for 10 mmBtu (installed, 1982)	$0.5/lb
Multiple Hearth	Requires afterburner; can't burn bulky solids, corrosives	Best for sludge incineration; low capital cost	Possible high maintenance costs; not energy efficient	N/A	N/A

Source: Engineering-Science (Reference 10).

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SECTION 11.0

EMERGING THERMAL TREATMENT TECHNOLOGIES

With the passage of the 1984 amendments to RCRA banning the land disposal of hazardous wastes, thermal treatment of hazardous wastes has become an increasingly attractive option. Accordingly, there has been a great deal of interest shown in the development of new technological approaches to thermal treatment. HWERL has identified 21 "innovative thermal processes for treating or destroying hazardous organic wastes", many of which are applicable to hazardous solvent wastes.[1]

Emerging technologies, by definition, are processes which provide an innovative or specialized approach to problems which have not been solved effectively by existing technologies. These technologies, therefore, may be more restricted by waste characteristics, technological complexity, or economic feasibility than the established systems. On the other hand, they may prove capable of achieving high destruction and removal efficiency (DRE) levels, an accomplishment not possible for some established technologies, or they may provide a radical improvement for a specific application. In general, these technologies have not been tested extensively on a full-scale basis.

Emerging thermal treatment technologies include modifications of conventional incineration technologies (e.g., the circulating bed incinerator) as well as more unconventional approaches to thermal destruction, e.g. the plasma arc pyrolysis system. Other emerging thermal systems such as wet air oxidation and supercritical water oxidation have been discussed above in the section dealing with chemical treatment processes. The technologies included here, and discussed below, are:

1. Circulating Bed Combustion
2. Molten Glass Incineration
3. Molten Salt Destruction
4. Pyrolysis Processes
5. In Situ Vitrification

11.1 CIRCULATING BED COMBUSTION

Circulating bed combustion (CBC) systems constitute an innovation in fluidized bed incineration technology. These systems utilize high air velocities and recirculating granular bed materials to maintain and achieve combustion of waste under fluidized bed conditions. The circulating bed material, serves to not only transfer heat energy and increase turbulence, but can be chosen for its chemical characteristics to bring about reaction and neutralization of certain products of combustion such as sulfur oxides and hydrochloric acid. CBC systems are applicable to solids, liquids, slurries, and sludges,[1] over a wide range of heat values and ash contents. Numerous performance tests have been conducted which indicate that circulating bed combustion can achieve very high destruction and removal efficiencies, while limiting other pollutant emissions to acceptable levels. CBC systems can offer both technological and economic advantages over established fluidized-bed incineration systems primarily due to the increased turbulence of the system. CBC systems operate at higher air velocities, and are not limited, as are fixed bed units, to the narrow range of design velocities needed to maintain fluidization while, at the same time, limiting entrainment and carry over of bed material.

11.1.1 Process Description

The circulating bed combustion process, depicted in Figures 11.1.1, represents design innovation to standard fluidized bed (FB) incineration systems. The CBC system is designed to handle all forms of waste, including solids, liquids, and sludges.

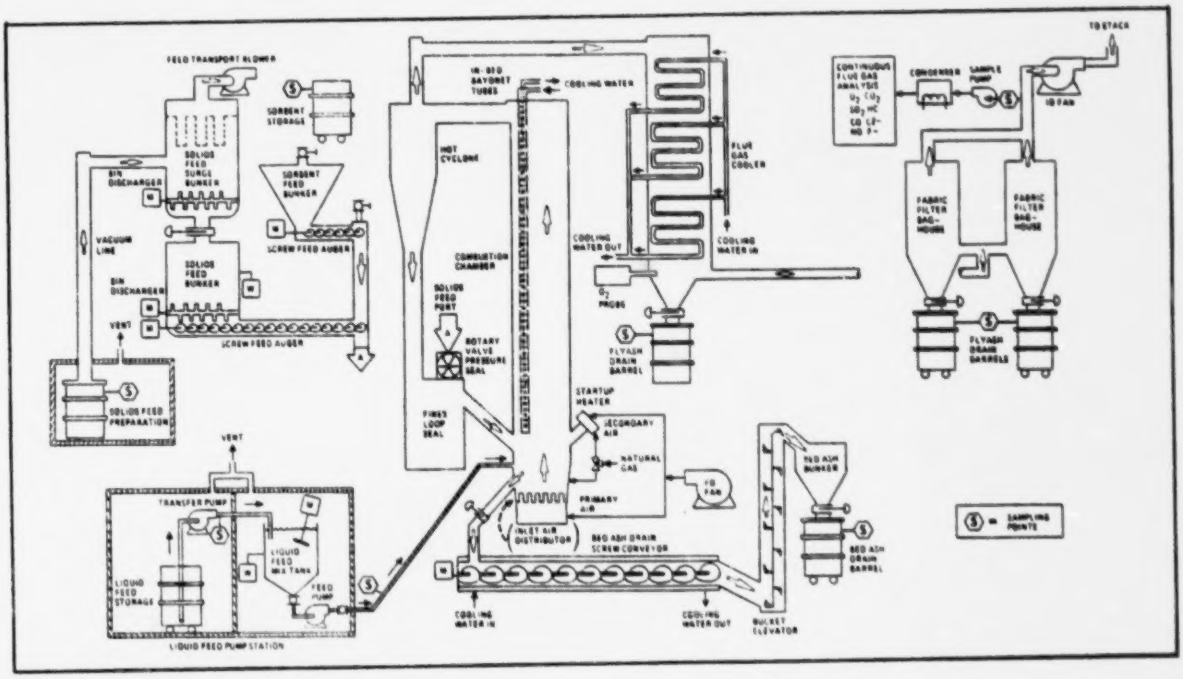


Figure 11.1.1. CBC incineration pilot plant located at GA Technologies.

Source: Reference 2.

The primary operating unit, the circulating bed combustor, incorporates a two-chamber design consisting of a combustion chamber and a hot cyclone chamber, as shown in Figure 11.1.1. The bed material used, limestone ($CaCO_3$), is fed to the system concurrently with the waste material. Limestone is used because it readily reacts with sulfur and chlorine compounds in the waste to form relatively innocuous salts such as $CaCl_2$ and $CaSO_4$. The general reaction scheme for the CBC process is as shown in Figure 11.1.2. Waste material is fed to the system either before the combustion loop for solids and sludges, or just at the start of the loop for liquids. As stated by the manufacturer, the CBC requires no specialized waste atomization or other injection mechanism, due to the inherently high level of turbulence in the system which ensures good distribution of waste feed.[3] During operation of the system, a high velocity stream of heated air (15 to 20 feet/sec.) entrains the material and carries it up the combustion column. As the waste flows upward, combustion occurs, and the byproducts are dispersed. The gaseous products, primarily CO_2 and water vapor, flow out the top of the combustor; the acidic byproducts such as HCl react with the limestone to form inorganic salts (generally these form as particulates); and, they and other solid byproducts flow downward through the hot cyclone, in which solids and gases are further separated. The hot flue gases pass first to a heat exchange system, then to a particulate control device, before being vented through the exhaust stack. Ash eventually settles within the combustion column and falls to a screw conveyor (as shown in Figure 11.1.1) where it is transported to ash recovery.

The circulating bed combustor is applicable to wastes with varying physical characteristics. Because the effectiveness of the design is based upon the development of a high degree of turbulence within the system, pretreatment systems are usually unnecessary to supplement dispersion of waste when fed (e.g., atomization of liquid wastes), or render wastes easier to disperse; e.g., crushing or grinding of solids.

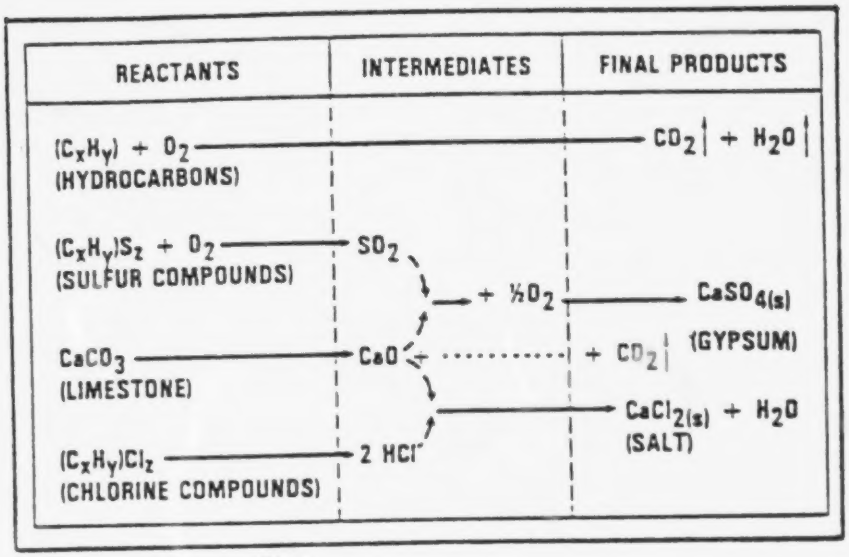


Figure 11.1.2. Chemical reactions that occur in CBC combustion chamber.

Source: Reference 2.

The operating conditions are as shown below.[1]

- Waste Feed: Applicable to any physical form - granular solids, liquids, sludges, slurries
- Temperature Range: 1400-1600°F (760-870°C)
- Residence Time:
  - Gas Phase: 2-3 seconds
  - Solids: 10 seconds to 10 hours.
- Capacity (lbs/hr): See Table 11.1.1
- Energy Type and Requirements:
  - Thermal: Sensible and latent heat; self-sufficient for wastes up to 85 percent water content
  - Electrical: Blower and feeder operation--approximately 30 HP for 2 MMBtu/hr incinerator

Input capacities, shown in Table 11.1.1, are dependent upon the type of waste fed to the unit. As noted the data were furnished by the developer; commercial units covering the range of capacities have not yet been constructed.

Waste streams of primary environmental concern in the CBC process are: (a) the acidic byproducts and organic products of incomplete combustion; and (b) hazardous heavy metals or other solid byproducts remaining in the ash. To date, performance testing has indicated that acid or PICs in the flue gas stream are not usually significant. The ash will be handled as a solid waste. If hazardous materials exist, they will be disposed of in an appropriate manner.[3]

11.1.2 Demonstrated Performance

A pilot-scale CBC was tested by the California Air Resources Board in cooperation with the manufacturer, GA Technologies, in 1983.[4] The testing involved a surrogate waste mixture which had a heating value of 8000 Btu/lb and included organic compounds such as xylene, ethylbenzene, toluene, hexachlorobenzene, Freon, and carbon tetrachloride. The CBC unit operated at a capacity of 0.5 MMBtu/hr, and a temperature of below 1600°F (870°C).

TABLE 11.1.1. CAPACITIES OF CBC SYSTEMS

Legend	Waste Description	Water Content %	Heat Content %	Throughput (lb/hr) vs. Combuster I.D.					
				16 in.	24 in.	36 in.	48 in.	60 in.	104 in.
	PCB Contaminated Soil	10	0	1,260	2,840	6,380	11,340	17,720	53,240
	PCB Contaminated Soil	20	0	930	2,080	4,680	8,320	13,010	39,130
	Chlorinated Chem. Sludge	80	1,331	440	1,000	2,250	4,000	6,250	18,770
	Chlorinated Chem. Sludge	40	4,000	340	770	1,740	3,100	4,840	14,530
	Chlorinated Liquid Waste	4	7,606	210	470	1,060	1,880	2,940	8,840
	Oil and Solvent Waste	13	11,227	130	280	640	1,140	1,780	5,340

Source: GA Technologies, Technical Bulletin.

A summary of results is shown in Table 11.1.2. Some of the conclusions drawn by Chang and Sorbo in Reference 4 are presented below:

1. The DRE of volatile and semi-volatile POHCs under less than optimum combustion conditions met RCRA requirements (99.99% DRE).

2. Total volatile PIC formation was found to correlate well with CO and THC, normalized to fuel flowrate (CO_2). Penetration of volatile chlorinated PICs (based on total chlorine content of the fuel) exceeded 1×10^{-4}. PIC benzene appeared in substantial concentrations in several samples and was not correlated with any conventional combustion parameters.

3. The DRE dropped sharply when the bed temperature fell below 700°C. Temperature appeared to be a major factor in the destruction of the fluorinated compounds and a moderate correlation between sulfur hexafluoride, DRE and temperature was observed.

4. The CBC seemed to behave as a plug-flow reactor, susceptible to pockets of non-stoichiometric air/fuel mixtures passing through the bed causing increased PIC formation. This observation suggests the importance of the fuel feed system on CBC performance and should be evaluated carefully by permitting authorities.

GA Technologies, the developer, has reported more than 7,500 hours of performance testing conducted under the auspices of DOE, EPRI (Electric Power Research Institute), TVA, and a number of commercial sponsors. The system has been tested with a variety of fuels and wastes to establish the combustion efficiency and the pollutant removal efficiency of the system relative to specific waste types. For solvent waste types, the system has generally shown a DRE above 99.99 percent, and an HCl capture of 99 percent and above. These tests were conducted at the company's 2×10^6 Btu/hr test unit in San Diego, CA. In summary, DREs found for POHCs existing in the organic wastes are as shown below:

Solvent	DRE	Temperature (°F)
Ethylbenzene	99.99	1600 (871°C)
Trichloroethane	99.999	1600
Vinyl chloride	99.9999	1600
1,2-trans-dichloroethylene	99.99	1600
1,2-dichloroethane	99.99	1600

Additional results, furnished by the developer,[2] GA Technologies, are shown in Table 11.1.3.

TABLE 11.1.2. SUMMARY OF BAG SAMPLE RESULTS

Bag Sample Concentration	Time								
Compound Name	0934-1035	1100-1124	1345-1418	1443-1623	1630-1705	1954-2054	2102-2140	2315-0020	0030-0100
POHCs - [ppb]									
Trichlorotrifluoroethane (Freon 113)	28	0.41	0.46	0.096	0.056	0.042	0.063	0.025	0.045
Average DRE (Penetration)	0.9994538 5.46E-04	0.9999950 4.98E-06	0.9999969 3.08E-06	0.9999987 1.33E-06	0.9999996 3.82E-07	0.9999994 5.81E-07	0.9999996 3.92E-07	0.9999997 3.17E-07	0.9999997 2.55E-07
Tetrachloromethane (Carbon tetrachloride)	0.31	0.33	0.24	0.47	0.21	0.22	0.27	0.92	1.4
Average DRE (Penetration)	0.9999952 4.75E-06	0.9999969 3.10E-06	0.9999987 1.26E-06	0.9999948 5.22E-06	0.9999989 1.13E-06	0.9999976 2.39E-06	0.9999987 1.32E-06	0.9999909 9.06E-06	0.9999938 6.23E-06
PICs - [ppb]									
Benzene	n.a.	7,400	n.a.	n.a.	n.a.	37,000	n.a.	n.a.	n.a.
Total Volatile PIC without Benzene - [ppb]	115.8	2034.1	4074.0	1528.4	611.9	2058.8	511.7	255.8	103.8
PIC-C1 - [ppb as C1]	129.8	2039.9	4079.4	1536.8	616.3	2063.8	515.7	258.9	108.4
(Volatile PIC-C1/C1-in)	1.33E-04	1.30E-03	2.87E-03	1.15E-03	4.42E-04	1.50E-03	3.38E-04	1.73E-04	6.46E-05
Fuel flowrate - [LB/HR]	52.7	83.3	74.6	68.4	73	56.2	61.2	70.1	78.5
Air flowrate - [DSCFM]	316	311	307	300	306	239	234	273	273
Total gas flow - [DSCFM]	347.6	342.1	337.7	330	336.6	262.9	257.4	300.3	300.3
Average 02 - [%]	10.8	6.8	4.4	5.8	4.9	5.8	7.7	7.3	8.0
Average CO2 - [%]	7.7	11.1	12.7	11.8	12.5	11.9	10.4	10.3	9.3
Average CO - [ppm]	1493	2630	2792	1406	738	1851	523	260	23
Average CO/CO2	2.10E-02	2.36E-02	2.07E-02	1.05E-02	5.66E-03	1.47E-02	4.89E-03	3.23E-03	2.56E-04
Average THC - [ppm]	38	384	321	224	194	240	n.a.	49	30
Average THC/CO2	4.40E-04	3.45E-03	2.45E-03	2.09E-03	1.51E-03	1.96E-03	n.a.	4.42E-04	3.21E-04

TABLE 11.1.3. TEST RESULTS ON HAZARDOUS WASTES CIRCULATING BED INCINERATOR PILOT PLANT

CHEMICAL FORMULA	CHEMICAL NAME	PHYSICAL FORM	DESTRUCTION EFFICIENCY, %	HCl CAPTURE, %	Ca/Cl$_2$ RATIO
CCl_4	CARBON TETRACHLORIDE	LIQUID	99.9992	99.3	2.2
$C_2Cl_3F_3$	FREON	LIQUID	99.9995	99.7	2.4
$C_{10}H_{19}O_6PS_2$	MALATHION	LIQUID	>99.9999 (UNDETECTABLE)	–	–
$C_{12}H_7Cl_3$	PCB	SOIL	>99.9999 (UNDETECTABLE)	99.1	2.2
$C_6H_4Cl_2$	DICHLOROBENZENE	SLUDGE	99.999	99	1.7
$C_8N_2H_4$	AROMATIC NITRILE	TACKY SOLID	>99.9999 (UNDETECTABLE)	–	–
C_2HCl_3	TRICHLOROETHENE	LIQUID	99.9999	99	1.7

Source: Reference 2.

11.1.3 Cost of Treatment

The costs of circulating bed incinerators according to GA Technologies Inc., are equivalent to the costs of conventional fluidized bed systems and less than those for rotary bed incinerators. Additional cost savings will also result from control of pollutants, such as those resulting from chlorine and sulfur in the waste, through addition of dry limestone to the bed. As shown in Table 11.1.3, chlorine capture efficiencies are reported to exceed 99 percent, a condition that meets EPA incinerator requirements. Presumably, other EPA requirements for air emissions, such as those existing for particulates and those being considered for toxics, can also be met and, thus, the expense of pollution control equipment can be reduced if not eliminated.

11.1.4 Status of Technology

Circulating bed combustion systems are in operation worldwide, for many process applications. There are no CBC incinerators operating specifically, however, as hazardous waste incinerators (although, as the manufacturer points out, many of the wastes disposed of by currently operating CBCs contain hazardous constituents). A listing of the operating units, submitted by the company, is shown in Table 11.1.4. GA Technologies is the only manufacturer of CBC technology.[3] In terms of market potential, the company provides the general comparison between existing technologies and CBC shown in Table 11.1.5.

While the CBC concept and available performance data are promising, additional data are needed to validate DREs and establish air emission levels for particulates, PICs, chlorine based pollutants, and other possible toxics. As noted in Reference 4, plug-flow reactor behavior, if it occurs, could lead to incomplete combustion and high emission levels of contaminants in the feed.

11.2 MOLTEN GLASS INCINERATION

Molten glass incinerators (MGI) are electric furnace reactors in which a pool of molten glass is used both as a means of destroying hazardous organic wastes and/or as a means for encapsulating the solid byproducts of hazardous waste treatment. The system utilizes furnaces similar to those used

TABLE 11.1.4. CIRCULATING BED COMBUSTION UNITS

Customer	Startup	Fuel	Output (MMBtu/hr)	Application
USA – GA				
GA Technologies Inc. San Diego, CA	1982 operating	Varied	2 MW (t)	Pilot plant
USA – Pyropower				
Gulf Oil Exploration Bakersfield, CA	1983 operating	Coal, coke, and limestone	50	Enhanced oil recovery
California Portland Cement Co. Colton, CA	1984 under construction	Coal and limestone	209	Cogeneration
B. F. Goodrich Henry, IL	1985	Coal and limestone	123	Process steam
Central Soya Chattanooga, TN	1985	Coal and limestone	105	Process steam
General Motors Corp. Pontiac, MI	1986	Coal, limestone, and plant wastes	370	Cogeneration
Colorado Ute Electric Utility Nucla, CO	1987	Coal and limestone	1000	Electrical generation
Foreign – Ahlstrom				
Hans Ahlstrom Laboratory Karhula, Finland	1976 operating	Varied	2 MW (t)	Pilot plant
Pihlava Board Mill Finland	1979 operating	Peat, wood, and coal	50	Cogeneration
Suonenjoki, Finland	1979 operating	Peat, wood, and coal	22	District heating
Kemira Oy, Finland	1980 operating	Zinciferous sludge	—	Sludge incineration
Kauttua, Finland	1981 operating	Peat, wood, and coal	220	Cogeneration

(continued)

TABLE 11.1.4 (continued)

Customer	Startup	Fuel	Output (MMBtu/hr)	Application
Foreign (cont'd)				
Hyvinkaa, Finland	1981 operating	Coal, peat, oil, and municipal wastes	85	District heating
Skelleftea, Sweden	1981 operating	Peat, wood, and coal	22	District heating
Ruzomberok, Czechoslovakia	1982 operating	Sewage sludge	—	Sludge incineration
Hylte Bruk, Sweden	1982 operating	Peat and coal	157	Cogeneration
Koskenkorva Distillery Finland	1982 operating	Peat and oil	63	Process steam
Kemira Chemical Finland	1982 operating	Peat and oil	173	Cogeneration
Zellstoff und Papierfabrik Frantschach AG Carinthia, Austria	1983 operating	Bark, brown coal, and sludge	188	Cogeneration
Ahlstrom Varkaus, Finland	1983 operating	Wood waste	68	Cogeneration–retrofit
Neste Lampo Oy Mantsala, Finland	1983 operating	Coal-water mixture and coal	10	Heating–firetube design
Bord Na Mona Ballyforan, Ireland	1984	Peat and oil	61	Cogeneration
Oriental Chemical Co. Inchon, Korea	1984	Petroleum, coke, and coal	330	Cogeneration
Ostersunds Fjarrvarme AB Ostersund, Sweden	1985	Peat, wood chips, and coal	85	Heating
Papyrus AB Kopporfors, Sweden	1985	Bark, peat, and coal	190	Cogeneration
Metsaliiton Teollisuus Oy Aanekoski, Finland	1985	Wood waste, peat, coal, and oil	258	Retrofit
Kereva Power Company Kereva, Finland	1985	Coal and limestone	102	Utility-heating

Source: Reference 2.

TABLE 11.1.5. CIRCULATING BED INCINERATOR VS. CONVENTIONAL INCINERATORS

Item	Circulating Bed	Bubbling Bed	Rotary Kiln
Cost			
Capital	$	$ + scrubber + extra feeders + foundations	$$ (double) + scrubber + afterburner
Operating	$	$ + more feeder maintenance + more limestone + scrubber	$$ + more auxiliary fuel + kiln maintenance + scrubber
Pollution control			
POHCs	In minimum-temperature combustor	In high-temperature combustor or afterburner	In afterburner
Cl, S, P	Dry limestone in combustor	Downstream scrubber	Downstream scrubber
NO_x, CO	Low due to turbulence, staged combustion	High: bubbles bypass and poor fuel distribution	High NO_x: hot afterburner
Upset Response	Slump bed; no pollution	Bypass scrubber pollution released	Bypass scrubber pollution released
Effluent	Dry ash	Wet ash sludge	Wet ash sludge
Feeding			
No. of Inlets	1-solid 1-liquid	5-solids 5-liquids	1-solids 2-liquids
Sludge Feeding	Direct	Filter/atomizer (5 each)	Filter/atomizer (2 each)
Solids Feedsize	Less than 1 in.	Less than ½ to ¼ in.	Larger, but shredded
Fly-Ash Recycle	Inherent (50 to 100 × feedrate)	Difficult mechanical/ pressure (10 × feedrate max)	Not done
Unit size			
Land area	Smaller	Larger (over 2×)	Larger (over 4×)
Efficiency			
Thermal, %	>78	<75	<70
Carbon, %	>98	<90	—
Feeder, hp	Minimum	High	High

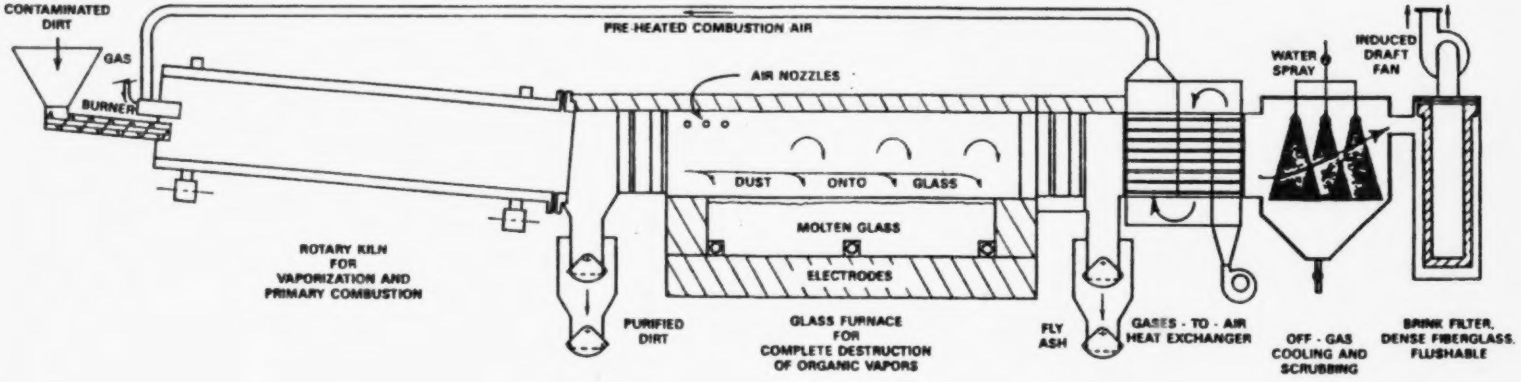
SI Conversion: mm = in. × 25.4

extensively in the glass manufacturing industry. Combustible hazardous wastes of virtually any physical form or chemical composition may be destroyed effectively in MGI systems. The system is considered particularly attractive for the destruction of highly toxic organic wastes, wastes containing heavy metals, and contaminated soils.[1] Solids introduced with the waste feed and many solid products of combustion become incorporated in a glass matrix, rendering them essentially environmentally inert and land disposable. Molten glass systems, are being studied by two separate firms (Battelle Northwest and Penberthy Electromelt International) as hazardous waste treatment devices. The process is considered to have certain technological and economic advantages over other established incineration technologies.[1]

11.2.1 Process Description

The molten glass furnace is a tunnel-shaped reactor, lined with refractory brick, in which a pool of glass is maintained in a molten state by electric current passing through the glass between submerged electrodes. Such furnaces are used extensively in the glass manufacturing industry. The unit is designed to withstand temperatures as high as 1260°C (2300°F), and corrosion by acidic gases. MGI systems, as designed, will be equipped with heat recovery and air pollution control systems, and can be combined with a preconditioning heater or primary incineration unit, as depicted in Figure 11.2.1.

In the absence of a primary incineration unit, wastes can be fed directly to the furnace chamber, above the pool of molten glass. Solids, slurries, and highly viscous liquids are usually charged via a screw feeder. Liquids may also be sprayed into the chamber through nozzles located at the top of the unit. Combustion air is fed to the system from two locations, one near the top (as shown in Figure 11.2.1), and the other nearer to the surface of the pool on the opposite side, in order to maximize the turbulence within the reaction space. The temperature within the chamber is maintained at 2300°F. Residence time of gases within the chamber is about 2 seconds although this can be increased if desired by reducing load. Residence time of solids within the glass will be appreciably longer, and is measured in terms of hours. Several furnace sizes accommodating various waste feed rates are available.[6]


CONTAMINATED DIRT
GAS
BURNER
PRE-HEATED COMBUSTION AIR
AIR NOZZLES
DUST ONTO GLASS
MOLTEN GLASS
ELECTRODES
WATER SPRAY
INDUCED DRAFT FAN
ROTARY KILN FOR VAPORIZATION AND PRIMARY COMBUSTION
PURIFIED DIRT
GLASS FURNACE FOR COMPLETE DESTRUCTION OF ORGANIC VAPORS
FLY ASH
GASES - TO - AIR HEAT EXCHANGER
OFF - GAS COOLING AND SCRUBBING
BRINK FILTER, DENSE FIBERGLASS, FLUSHABLE

	BY	DATE	PENBERTHY ELECTROMELT INTERNATIONAL, INC. 631 SOUTH 96th STREET SEATTLE, WASHINGTON 98108
DRAWN	R. Knowles	12-5-84	
CHECKED			
ENGINEER	L. Penberthy		
APPROVED	LP		DR'W'G NO.:
ISSUE DATE	7DEC84		8181 PLUS 8180

Figure 11.2.1. Dirt purifier and hazardous waste incinerator.

Source: Reference 7.

During operation, volatile waste materials mix with air, ignite, and react in the space above, and at the surface of, the pool of molten glass. The solid products of combustion, dirt, and other noncombustible materials (e.g., heavy metal contaminants or the solid waste being treated) will be incorporated into the glass bed. Gaseous products flow out of the chamber, through a series of ceramic fiber filters, which catch most of the particulate matter. The hot gases, consisting primarily of CO_2, water vapor, and HCl (if chlorinated organics are incinerated) then pass through a heat exchanger for heat recovery (heat is used to warm the combustion air, as shown in Figure 11.2.1). The exhaust gases flow next to a series of water spray-type scrubbers. The first spray chamber is designed to use a slightly alkaline scrubbing liquor, to capture acidic vapors. Water is used in the other spray chamber (or chambers), to remove remaining particulates and other scrubbable vapors. The gases are then reheated above the dewpoint, and passed through charcoal and HEPA filters before being vented out the stack. The entire system is maintained under negative pressure by means of the exhaust blower.[7]

After a period of usage, the molten glass bed, with the solid waste materials incorporated, is tapped out of the chamber into metal canisters, and, after cooling, is sent to a disposal facility. The ceramic filters, which eventually become loaded with particulate matter, can be disposed of by dissolving them in the molten glass bed. The glass bed can also be used to encapsulate the sludge from the spray chambers, and the spent charcoal and HEPA filters.

Major advantages of the molten glass incineration system are its applicability to many forms of hazardous waste and the encapsulation of residuals in a nonleachable glass matrix. Performance testing, and data generated from commercial usage of MGI units in the chemical processing industry, while limited, have shown no significant difference in the effective operation of such systems for wastes of different physical forms and widely varying chemical composition. However, preheating and chemical treatment of wastes are often used to aid combustion and reduce system maintenance and down time. The waste related factors which may be of the greatest particular concern are moisture content and metals and inorganics content. The significance of these characteristics are discussed in detail below.

11.2.1.1 Moisture Content--

A high concentration of water in waste will necessitate additional energy input to the system and may affect destruction efficiencies. Penberthy has set a moisture content limit of 20 percent (by weight) for its systems.[6] Since many solvent wastes contain water at levels higher than this, pretreatment of the waste will be needed. Pretreatment systems which can be used include evaporation and sedimentation. Dewatering options may be somewhat limited for certain solvent wastes, due to characteristics such as volatility and miscibility with water.

11.2.1.2 Metal Content--

Metals and minerals which are constituents of wastes pose a problem to the effective operation of molten glass incinerators. Those materials which are denser than the molten glass will tend to accumulate near the bottom of the furnace. (Battelle reports that its process, which involves intermixing of molten glass and waste, achieves 95 percent detention of nonvolatile heavy metals.)[1] Eventually, due to their electrolytic properties, they may affect the operation of the metal electrodes. Penberthy has recommended the usage of sumps to collect and localize settling particles of metal. Such systems have been found to be effective in reducing the effect of metals on furnace operation.[7]

11.2.2 Demonstrated Performance

No data, demonstrating DREs or quantifying exhaust gas emissions, are available for solvent wastes or any other wastes. These data are needed if this technology, which appears promising in concept, is to be utilized for hazardous waste treatment.

11.2.3 Cost of Treatment

Costs will depend to an appreciable extent upon the need for pretreatment and the demands placed on the system used to clean exhaust gases.

11.2.4 Status of Technology

Molten glass incinerators are available commercially from Penberthy Electromelt International Inc. for use as chemical processing units. Battelle Northwest, another company involved in the development of MGI systems, has not yet produced equipment on a commercial scale. The Penberthy system has not been sold or permitted specifically as a hazardous waste incinerator to date. However, despite the lack of information concerning its application to hazardous wastes the technology would appear to offer certain definite advantages. Anticipated advantages are as follows:

- Able to achieve significant waste volume reduction
- Able to destroy almost all forms of hazardous waste, largely independent of physical state or chemical composition
- Operation at high temperature, thus particularly attractive for highly toxic organic streams and wastes containing long-chain resinous organics
- Heat recovery and air pollution control built into system
- Solid byproducts transformed via glass encapsulation to environmentally safe state. The encapsulates are resistant if not inert to chemical reaction, leaching, and fracture. They probably can be disposed of in landfills
- System is small in size, can be transportable
- Equipment used is relatively simple, representing basic technology that has been applied in heavy industry for 30 years

Limitations, also largely conjectural at this stage, include the following:

- Unproven technology. There is no knowledge of long term operation and maintenance requirements, or how performance would be affected by long term usage with wastes
- Energy costs and capital costs are relatively high
- Control system as described may be inadequate for exhaust gases of the type anticipated from hazardous waste destruction

11.3 MOLTEN SALT DESTRUCTION

Molten salt incinerators involve the combustion of waste materials in a bed of molten salt. Using the molten salt incineration process, "organic wastes may be burned while, at the same time scrubbing in situ any objectionable byproducts of that burning and thus preventing their emission in the effluent gas stream."[8] Molten salt incinerators were developed by Rockwell International, specifically to burn hazardous organic wastes and, as designed, are applicable to both liquid and solid waste streams. However, wastes with high ash content or a high percentage of water or noncombustible material are not good candidates for molten salt destruction.

11.3.1 Process Description

The molten salt destruction process has been under development by Rockwell International since 1969.[9] The original intent was to use the process to gasify coal. A variety of salts can be used, but the most recent studies have used sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) in the 1,450°F to 2,200°F (790°C to 1200°C) temperature range.

In addition to the Rockwell process, another molten salt process is under development. The State of New Jersey in late 1982 issued a contract to the Questex Corporation of New York to evaluate a mobile, offsite earth decontaminator (MOSED), a waste treatment unit based on the molten salt destruction principle. A status report on the development of this device was presented at the 1985 Hazpro Conference.[10]

As shown in a schematic of the Rockwell process (Figure 11.3.1), the waste is fed to the bottom of a vessel containing the liquid salt along with air or oxygen-enriched air. The molten salt is maintained at temperatures of 800-1,000°C (1,500 to 1,850°F).[11] The high rate of heat transfer to the waste causes rapid destruction. Hydrocarbons are oxidized to carbon dioxide and water. Constituents of the feed such as phosphorous, sulfur, arsenic, and the halogens react with the salt (i.e., sodium carbonate) to form inorganic salts, which are retained in the melt.[11] The operating temperatures are low enough to prevent NO_x emissions.[1,9]

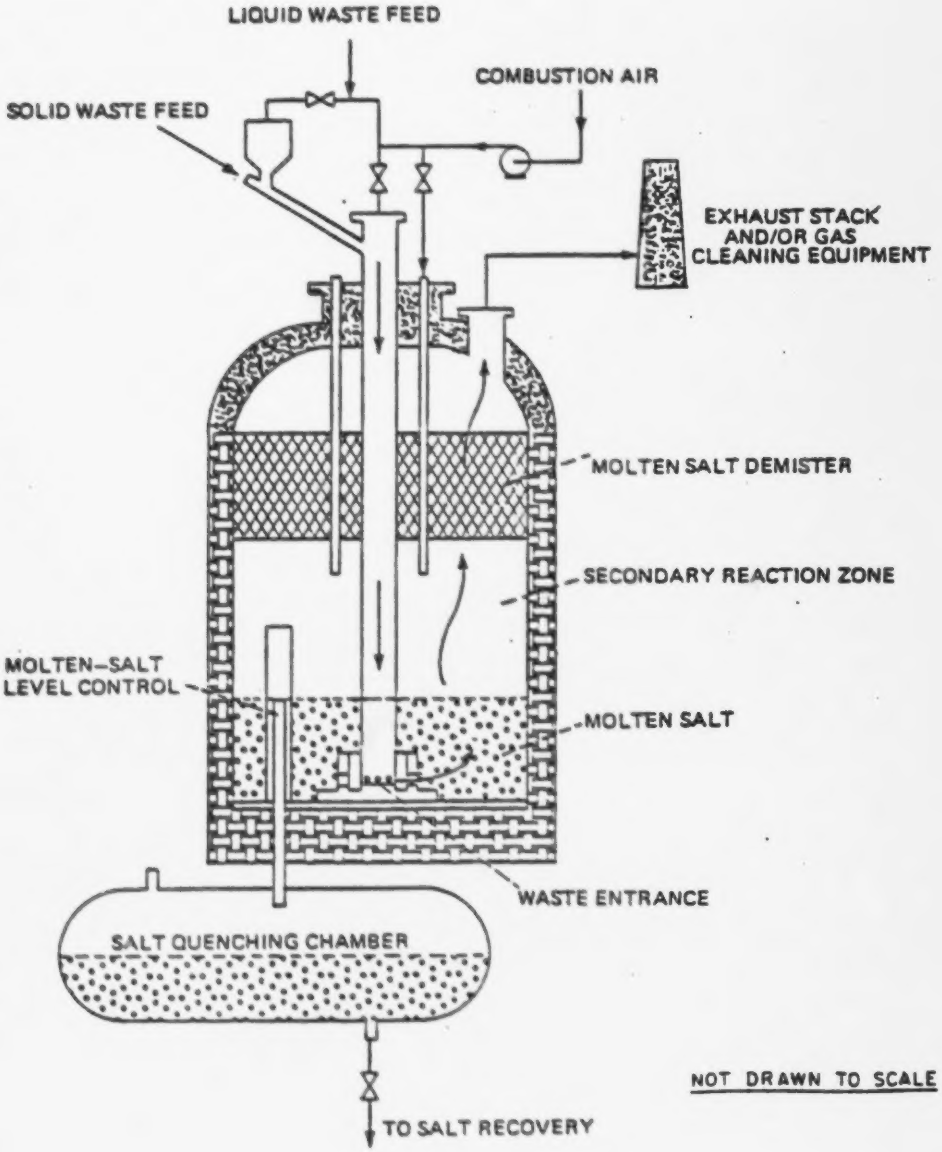


Figure 11.3.1. Molten Salt Combustion System.

Source: Reference 8.

Eventually, the build-up of inorganic salts must be removed from the molten bed to maintain its ability to absorb acidic gases. Additionally, ash introduced by the waste must be removed to maintain the fluidity of the bed. Ash concentrations in the melt must be below 20 percent to preserve fluidity.

Melt removal can be performed continuously or in a batch mode. Continuous removal is generally used if the ash feed rates are high. The melt can be quenched in water and the ash can be separated by filtration while the salt remains in solution. The salt can then be recovered and recycled. Salt losses, necessary recycle rates, and recycling process design are strongly dependent on the waste feed characteristics.[1,9]

11.3.1.1 Waste Characteristics and Pretreatment Requirements--

Molten salt destruction (MSD) systems are limited in their applicability to various hazardous wastes. Although the system is capable of handling hazardous wastes in both the liquid and solid state, MSD is in practice limited to the incineration of hazardous organic wastes which have a relatively low percentage of solids or inorganics. Slurried wastes and most "dry" solid wastes (e.g., contaminated soils) are not good candidates for incineration by MSD. When ash accumulates in the bed, it tends to form a waste matrix, which eventually affects bed fluidity, the overall transfer of heat and will eventually limit waste byproduct neutralization within the molten mass. Thus, 20 percent was determined to be the limit to which the system could effectively operate.[11]

Wastes with high water content may pose a problem to the effectiveness of the molten salt destruction process. As moisture content increases, the waste will require more fuel and combustion air, to the point where the reactor volume is limited. Thus, many wastes must be dewatered by pretreatment to ensure that they are effectively destroyed in the MSD.

Discussion with Rockwell indicated that there is no established pretreatment system designed as part of the MSD system. However, separation technology for removal of solids and to dewater wastes prior to incineration in a MSD unit must be considered.

11.3.1.2 Operating Parameters--

The operating parameters for a molten salt unit are:

- Temperature Range: 800-1000°C (1500-1850°F)
- Residence Time:
  - Gas Phase: approx. 5 seconds
  - Liquid or Solid Phase: hours
- Energy Requirement: Natural gas or oil to heat salt bed; Auxiliary fuel for noncombustible wastes; Power for exhaust
- Available Capacity: commercial units available at 2000lbs/hr; Pilot scale in use operating at 250lbs/hr.
- Operating Limitations: Heat generation. MSD requires a cooling system for the overall unit to prevent operational failures

11.3.1.3 Post-Treatment Requirements--

Although post-treatment requirements have not yet been defined, it is likely that treatment will be required to remove products of combustion that are not scrubbed out of the exhaust gases by the molten salt. These products of combustion could include particulates, POHCs and PICs. Solid residues (i.e., used salt) must be reprocessed or disposed.

11.3.2 Demonstrated Performance

Rockwell International has built two bench scale combustors (0.5 to 2 lb/hr), a pilot plant (55 to 220 lb/hr), and a portable unit (500 lb/hr) (Edwards, 1983). They have also built a 200 lb/hr coal gasifier based on the molten salt process. Destruction efficiency tests have been conducted at the bench and pilot scale levels. While no data were found to demonstrate the DRE of the molten salt destruction technology for the solvents of concern, data showing five nines to eleven nines DRE for certain organic compounds have been obtained.

Many wastes have been tested in the bench scale unit. Chemical warfare agents GB, Mustard HD, and VX have been destroyed at efficiencies ranging from 99.999988 to 99.9999995 percent. Other chemicals that have been destroyed using the molten salt combustion process include: chlordane, malathion, Sevin, DDT, 2,4-D herbicide, tar, chloroform, perchloroethylene distillation bottoms, trichloroethane, tributyl phosphate, and PCBs.[9]

The PCB trial combustion data are presented in Table 11.3.1. The destruction efficiency at the lowest operating temperature 700°C (1,300°F) exceeded 99.99995 percent. The average residence time of the PCB in the melted salt was 0.25 to 0.50 seconds, based on gas velocities of 1 to 2 ft/sec through the 0.5 ft of melt.[9]

Hexachlorobenzene (HCB) and chlordane destruction were tested in the pilot plant facility.[12] Feed rates for HCB and chlordane were as high as 269 lb/hr and 72 lb/hr, respectively. Bed temperatures ranged from 1,685° to 1,805°F (920°C to 985°C) and residence times were in the 2 to 3 second range. HCB destruction efficiencies ranged from 99.9999999 to 99.999999999, and chlordane destruction efficiencies ranged from 99.99999 to 99.999999). The results of the pilot-scale tests are summarized in Table 11.3.2.

As shown in Table 11.3.2, very high DREs were noted for both compounds. HCl emissions were below 100 ppm, and no Cl_2 gas or phosgene gas was detected. Particulate emissions were measured, but were found to be quite low, and analysis showed that particulate matter was nonhazardous. The improved performance in the pilot scale reactor was attributed to greater residence times.

11.3.3 Costs of Treatment

Detailed estimates of costs for molten salt destruction have not been formulated. Based on the performance of the bench- and pilot-scale MSD units, it is speculated that general operating costs will be low, but that the initial capital costs will be high. Molten salt destruction operating costs should be lower than established technologies such as rotary kilns. Operating temperature are low and the system needs not have a complex air pollution control system and associated appurtenances, (although emission data are needed to verify this), or ash recovery and transport systems.

TABLE 11.3.1. PCB COMBUSTION TESTS IN SODIUM-POTASSIUM-CHLORIDE-CARBONATE MELTS [Edwards, 1983]

Temp (°C)	Stochiometric air (%)	Concentration of KCl, NaCl in melt (wt %)	Extent of PCB destruction[a] (%)	Concentration of PCB in off-gas[a] (μg/m^3)
870	145	60	>99.99995	<52
830	115	74	>99.99995	<65
700	160	97	>99.99995	<51
895	180	100	>99.99993	<59
775	125	100	>99.99996	<44
775	90	100	>99.99996	<66

[a] PCBs were not detected in the off-gas, i.e., values shown are detection limits.

Reference: Reference 9.

TABLE 11.3.2. SUMMARY OF PILOT-SCALE TEST RESULTS

	PCB	Chlordane
Combustor Feed Rate (lb/hr)	20.9 - 122.0	12.1 - 32.7
Combustor Off-gas		
- mg/m^3	$2.7 \times 10^{-4} - 7.1 \times 10^{-2}$	$5.3 \times 10^{-3} - 6.8 \times 10^{-2}$
- ppmv	$2.3 \times 10^{-5} - 6.1 \times 10^{-3}$	$3.2 \times 10^{-4} - 4.1 \times 10^{-3}$
Baghouse		
- mg/m^3	$<6 \times 10^{-6} - 1.6 \times 10^{-4}$	$<3.6 \times 10^{-4} - <4.4 \times 10^{-3}$
- ppmv	$<5.2 \times 10^{-7} - 1.4 \times 10^{-5}$	$<2.1 \times 10^{-5} - <2.6 \times 10^{-4}$
Spent Melt (ppmv)	0.001 - 0.104	0.0044 - 1.2
NO_x (ppmv)	70 - 125	0.5 - 630
HC (ppmv)	35 - 110	0.4 - 60
Particulate (mg/m^3)	$<6.2 \times 10^{-3} - 0.107$	$4.1 \times 10^{-3} - 1.75 \times 10^{-2}$
DRE (%)	11-9's - 9-9's	8-9's - 7-9's

Note: The pH of the liquid in a small sampling scrubber in the off-gas line remained basic throughout the test indicating essentially no HCl emission.

Source: Reference 1.

11.3.4 Status of Technology

Molten salt destruction systems are a proprietary design of the Rockwell International Corporation. Rockwell began development of the MSD system in 1969, obtaining several patents for the technology. By 1980, the system was made available for commercial-scale application, at a capacity of 2000 lbs/hr. for destruction of specific waste types. The company constructed, and currently maintains three different sized units, including a bench-scale (2 lbs/hr) unit, and a pilot-scale (200 lb/hr) unit, and a full scale (2000 lbs/hr) unit, for demonstration of molten salt incineration capabilities. However, no commercial scale units have been sold by the company to date. Rockwell has indicated that development of this technology has been curtailed, due in part to the limited demand encountered. Rockwell will maintain their demonstration units and considers future development of MSD a possibility.[11]

As demonstrated in the molten salt destruction process performance tests, MSD systems have certain distinct advantages as an incineration technology alternative. The limitations of the system however, may prove to severely limit its further development.

Advantages--

- Achievement of high destruction efficiencies for many wastes, including highly toxic and highly halogenated wastes;
- Low NO_x and heavy metal emissions
- Retention of halogens and metals in a manageable salt matrix;
- Compact size. The process has few moving parts; and acts as its own, highly efficient scrubber for acid combustion gases;
- Especially well-suited to wastes whose combustion results in liberation of acids;
- Improved reliability due to simple design;
- Increased waste throughput possible

Limitations--

- Generally restricted to certain types of organic hazardous wastes;
- Sensitive to high (20%) ash content in wastes;
- Molten salt is corrosive to all but specific engineering alloys. Material and construction costs will therefore be high, and management of spent salt beds will be difficult;
- No commercial applications to date, thus, no existing record of long-term performance and operation and maintenance requirements

11.4 PYROLYSIS PROCESSES

Pyrolysis reactors are systems in which destruction of waste contaminants is accomplished by applying a large thermal input resulting in molecular decomposition, often down to an elemental or simple molecular form. No oxidation reactions are involved in these processes. Pyrolysis reactors can achieve very high destruction efficiencies for wastes, including difficult to dispose of wastes such as dioxin wastes. A variety of pyrolysis systems have been developed, including continuous and batch furnace pyrolyzers, the plasma arc reactor, and the high temperature fluid wall reactor. These are described below.

11.4.1 Furnace Pyrolysis Systems

11.4.1.1 Process Description--

The pyrolysis system shown in Figure 11.4.1 consists of three major components: a continuous rotary furnace, a rich fume secondary combustion chamber, and a heat recovery unit. The furnace is similar to furnaces employed to treat metals and other materials requiring controlled thermal treatment. Waste is continuously fed to a rotating belt which passes through an indirect-fired, oxygen-free pyrolytic chamber. The waste is heated to between 540°C (1000°F) and 870°C (1600°F). Volatiles in the waste or resulting from pyrolysis are driven off leaving behind inert materials, metals, and other inorganics, which are continuously removed from the moving belt. The volatile gases, containing organic compounds and products of pyrolysis such as H_2 and some HCl (if chlorine is present in the waste) are

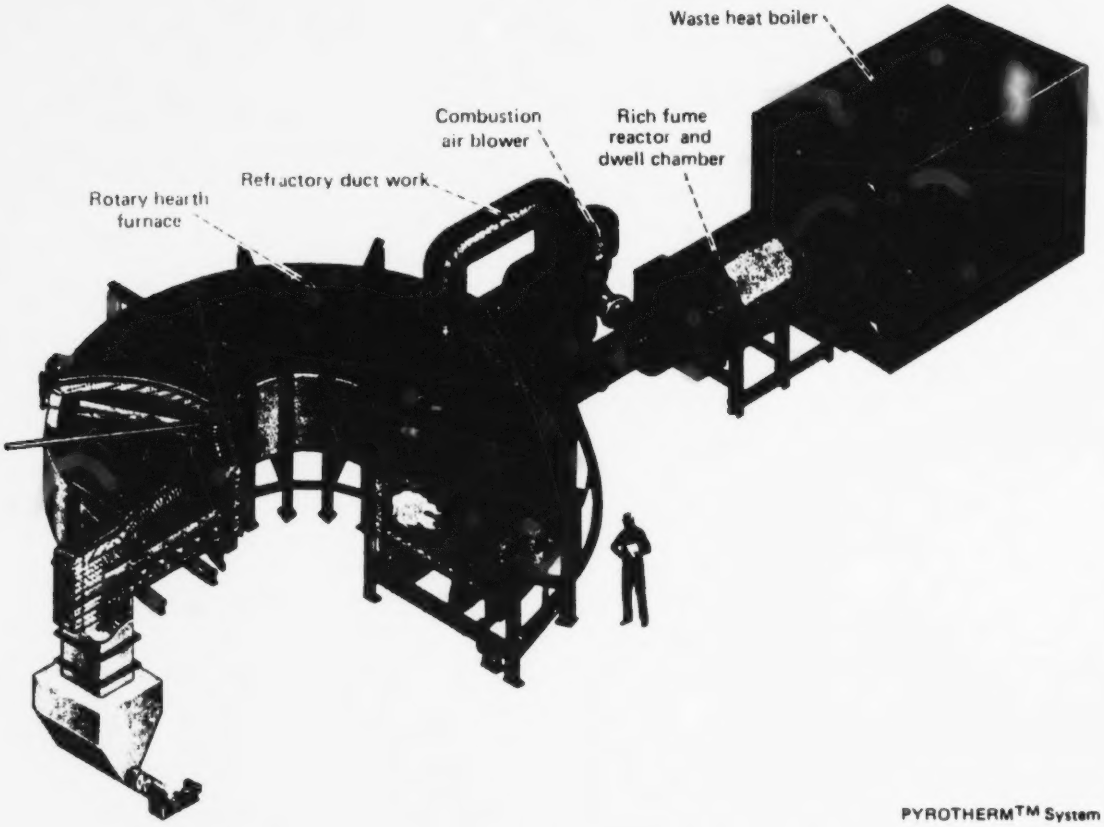


Figure 11.4.1 Continuous Pyrolyzer

Source: Reference 13

combusted in the rich fume reactor to complete the destruction of any organic materials present, and then flow through a waste heat boiler or a similar device used to recover energy. Although, some HCl formed by pyrolysis is removed through contact with alkaline components (either in the waste or added to the feed deliberately for that purpose) it is conceivable that some type of air pollution control device might be needed to control acid gas emissions. Reportedly other pollutants such as particulates and nitrogen oxides will not be a problem because of the low turbulence level within the pyrolysis chamber and the reducing atmosphere of pyrolysis, respectively.

Although wastes with a wide range of chemical characteristics may be treated in a pyrolytic incinerator, certain wastes are clearly better candidates than others. As noted by Midland-Ross, the developer,[13] pyrolysis systems work best for wastes which fall into the following categories:

> "1. Too viscous to atomize in liquid incinerators, yet too fluid for spreader-stoker incinerators.
>
> 2. Low melting point materials that foul heat exchangers, spall refractories, and complicate residue discharge.
>
> 3. High residue materials (ash), with easily entrained solids, that would generally require substantial stack gas cleanup.
>
> 4. Material containing priority pollutants with excessive vapor pressure at incineration temperatures.
>
> 5. Any material, drummed or loose bulk, where controlled thermal treatment is desired to make clean gases for heat recovery or for discharge to the atmosphere."

Operating conditions for the components of the two types of pyrolyzers (batch and continuous) produced by Midland-Ross are as follows.[1]

Pyrolyzer

- Temperature Range: 650°-870°C (1200°-1600°F)
- Residence Time Range: 15-30 minutes (continuous systems) 4-6 hours (batch systems)
- Auxiliary Fuel Requirements: Natural gas, fuel oils, and/or electrically-fired

Rich Fume Incinerator (Reactor)

- Temperature Range:	980°-1200°C+ (1800°-2200°F+)
- Residence Time Range:	1.0-2.0 seconds

Commercial System

- PyroBatch Systems	1,000 lb/load to 30,000 lb/load
- PyroTherm Systems	500 lb/h up

11.4.1.2 Demonstrated Performance--

A Midland-Ross batch pyrolysis system, operated by the McDonnell Douglas Company in St. Charles, Missouri, was RCRA permitted in 1984 after a series of trial burns using wastes with five POHCs with 50-70 percent chlorinated hydrocarbons. Average DREs for the five POHCs during the trial burns were 99.9999 percent (six nines). Removal efficiency for HCl was 99.9 percent, and particulate emissions were 0.035 grains per dry standard cubic foot.(1) No other data appear to be available.

11.4.1.3 Cost of Treatment--

As noted in Reference 1, the developer states the following with regard to cost.

> "Our cost estimates are proprietary information and are supplied only to customers with whom we have projects. To date, most of our clients' wastes applications are different from one another, hence project capital costs are also different. However, inherent benefits of pyrolytic incineration help our clients realize significant overall project cost reductions relative to direct incineration systems."

11.4.1.4 Status of Technology--

As noted, both batch and continuous pyrolysis are supplied commercially by the Midland-Ross Corporation. The company also maintains a research facility and offers complete bench and pilot test facilities.

The pyrolysis systems are particularly suited for sludges and solid wastes because of the long residence times that can be employed to assist destruction.[14] In addition to the potential to destroy all organics and to handle difficult waste types, pyrolysis systems, as noted by the developer, offer the following advantages.[1]

1. Salts and metals (inert materials) with moderate melting points are not liquified because the pyrolyzer operates at a design temperature below the melting points of most salts and metals.
2. Since the same salts and metals are normally not vaporized, refractory spalling, surface fouling, and formation of inert aerosol condensates are all greatly reduced.
3. Particulate emissions with most types of pyrolyzers are greatly reduced because the waste is not agitated or contacted with turbulent gases during pyrolysis, so particulate cleanup devices in many cases are not needed to meet Federal standards.
4. Waste-borne NO_x is reduced in a pyrolysis atmosphere to N_2 and H_2O. Hence, NO_x emissions from the process are considerably lower.
5. Chlorinated or halogenated materials (e.g., hydrochloric acid) typically liberated by thermal treatment of a waste can be adsorbed by caustics present in, or added to, the feed prior to pyrolysis. This often leads to a reduction in emissions of HCl and SO_X from 50 to 90 percent.
6. Leaching of metals and salts from the carbonaceous residue (char) is reduced because they are exposed to a reducing atmosphere throughout the process, and they tend to be physically or chemically tied up in the char.
7. Overall, gas cleanup equipment is greatly reduced or not required to pyrolytically treat the same waste materials treated by direct incineration.

11.4.2 Plasma Arc Pyrolysis

11.4.2.1 Process Description--

In this process, under development by Pyrolysis Systems Inc. of Welland, Ontario, waste molecules are destroyed by the action of a thermal plasma field. The field is generated by passing an electric charge through a low pressure air stream thereby ionizing the gas molecules and generating temperatures up to 10,000°C.

A flow diagram of the plasma pyrolysis system is shown in Figure 11.4.2. The plasma device is horizontally mounted in a refractory-lined pyrolysis chamber with a length of approximately 2 meters and a diameter of 1 meter. The colinear electrodes of the plasma device act as a plug-flow atomization zone for the liquid waste feed, and the pyrolysis chamber serves as a mixing zone where the atoms recombine to form hydrogen, carbon monoxide, hydrogen chloride, and particulate carbon. The approximate residence times in the atomization zone and the recombination zone are 500 microseconds and 1 second, respectively. The temperature in the recombination zone is normally maintained at 900-1,200°C (1650°F - 2190°F).[16]

After the pyrolysis chamber, the product gases are scrubbed with water and caustic soda to remove hydrochloric acid and particulate matter. The remaining gases, a high percentage of which are combustible, are drawn by an induction fan to the flare stack where they are electrically ignited. In the event of a power failure, the product gases are vectored through an activated carbon filter to remove any undestroyed toxic material.

The treatment system that is currently being used for testing purposes is rated at 4 kg/minute of waste feed or approximately 55 gal/hour. The product gas production rates are 5-6 m^3/minute prior to flaring. To facilitate testing, a flare containment chamber and 30 ft. stack have also been added to the system. The gas flow rate at the stack exit is approximately 36 m^3/minute.[16]

A major advantage of this system is that it can be moved from waste site to waste site as desired. The entire treatment system, including a laboratory, process control and monitoring equipment, and transformer and switching equipment, are contained on a 45 ft. tractor-trailer bed.[16]

Two residual streams are generated by this process. These are the exhaust gases that are released up the stack as a flare, and the scrubber water stream. Since the product gas (after scrubbing) is mainly hydrogen, carbon monoxide, and nitrogen, it burns with a clean flame after being ignited. Analysis of the flare exhaust gases, presented in the following section, indicates virtually complete destruction of toxic constituents.

The scrubber water stream is composed mainly of salt water from neutralization of HCl and particulates, primarily carbon. Analyses of the scrubber water for the waste constituent of concern (e.g., carbon

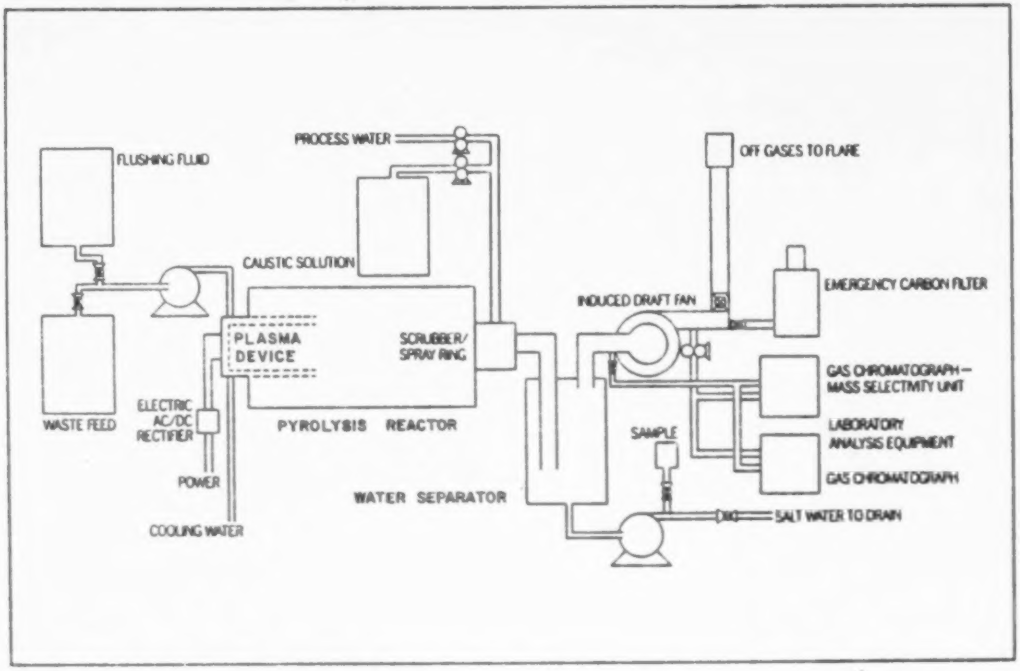


Figure 11.4.2. Pyroplasma process flow diagram.

Source: Reference 15.

tetrachloride (CCl_4) and PCB in the feed material) have shown that the constituents were present at low ppb concentrations. The quality of scrubber water generated would depend on the water feed rate and corresponding product gas and scrubber waste flowrates. During a test in which 2.5 kg/min of waste containing 35 to 40 percent CCl_4 was fed to the reactor, a scrubber water effluent flowrate of 30 l/minute was generated.[15]

The reactor as it is currently designed can only be used to treat liquid waste streams with viscosities up to that of 30 to 40 weight motor oils. Particulates are removed by a 200 mesh screen prior to being fed into the reactor. Contaminated soils and viscous sludges cannot be treated.

11.4.2.2 Demonstrated Performance--

The plasma arc system has been tested using several liquid feed materials, including carbon tetrachloride (CCl_4), polychlorinated biphenyls (PCBs), and methyl ethyl ketone (MEK).

Table 11.4.1 presents the results of three test burns conducted in Kingston, Ontario using carbon tetrachloride in the feed material. The carbon tetrachloride was fed to the reactor along with ethanol, methyl ethyl ketone, and water at a rate of 1 kg of CCl_4/minute. The duration of each of these tests was 60 minutes, and stack gas flowrates and temperatures averaged 32.5 dry standard cubic meter/minute (dscm/min) and 793°C (1460°F), respectively. As can be seen in the table, the destruction and removal efficiency (DRE) of CCl_4 in each of the tests was high, exceeding six nines. In addition, the concentration of HCl in exhaust gases was less than the upper limit of 1.8 kg/hr required by RCRA guidelines. The only possible area of concern is that the concentration of CCl_4 in the scrubber water is greater than 1 ppb. As far as PCBs are concerned, the destruction and removal efficiency in each of the tests was greater than 6 nines, and in some cases reached 8 nines. Similar or better results can be anticipated for most solvents of concern.

11.4.2.3 Costs of Treatment--

The approximate capital cost of a unit similar to the one tested would be in the range of 1 to 1.5 million dollars.[16] More accurate figures will be available once a commercial unit has been built.

TABLE 11.4.1. CARBON TETRACHLORIDE TEST RESULTS

Parameter	Test 1	Test 2	Test 3
Chlorine Mass Loading (%)	35	40	35
Scrubber Effluent			
CCl_4(ppb)	1.27	5.47	3.26
mg/hr	2.29	9.85	5.87
Flare Exhaust			
CCl_4(ppb)	0.83	0.43	0.63
mg/hr	12.1	4.9	7.2
NO_x			
ppm(v/v)	106	92	81
lbs/hr	1.02	0.69	0.02
CO			
ppm(v/v)	48	57	81
lbs/hr	0.28	0.26	0.37
HCl			
mg/dscm	(1)	137.7	247.7
kg/hr	(1)	0.25	0.44
Destruction Removal Efficiency	99.99998	99.99998	99.99998

Source: Reference 15.

11.4.2.4 Status of Technology--

The construction and testing of the plasma arc system is jointly sponsored by the New York State Department of Environmental Conservation (NYDEC) and the U.S. EPA Hazardous Waste Engineering Research Laboratory (HWERL). The project is comprised of four phases, which are:

Phase 1: Design and construction of the mobile plasma arc system by the contractor, Pyrolysis Systems, Inc. (PSI).

Phase 2: Performance testing of the plasma arc system at the Kingston, Ontario, Canada test site.

Phase 3: Installation of the plasma arc system and additional performance testing at Love Canal, Niagra Falls, N.Y.

Phase 4: Demonstration testing, as designated by NYDEC.

Phase 1 took place in 1982 and Phase 2, the results of which have been presented above, was completed in early 1986. Phase 3 will be initiated later in 1986.

The plasma technology is being jointly marketed by Westinghouse Electric Corporation Waste Technology Services Division and PSI. Once the system has been properly tested, they plan to lease these units to companies or organizations that require the system for waste clean up. The current system is only designed to handle liquid wastes. Future plans by PSI and Westinghouse include the design of units which could handle contaminated soil and other solid wastes.[17]

11.4.3 High Temperature Fluid Wall (HTFW) Destruction - Advanced Electric Reactor

11.4.3.1 Process Description--

The HTFW factor was originally developed by Thagard Research of Costa Mesa, California. However, the J.M. Huber Corp. of Borger, Texas has developed proprietary modifications to this original design. The reactor, called the Advanced Electric Reactor (AER), is shown in Figure 11.4.3. The reactor is a thermal destruction device which employs radiant energy provided by electrically heated carbon electrodes to heat a porous reactor core. The

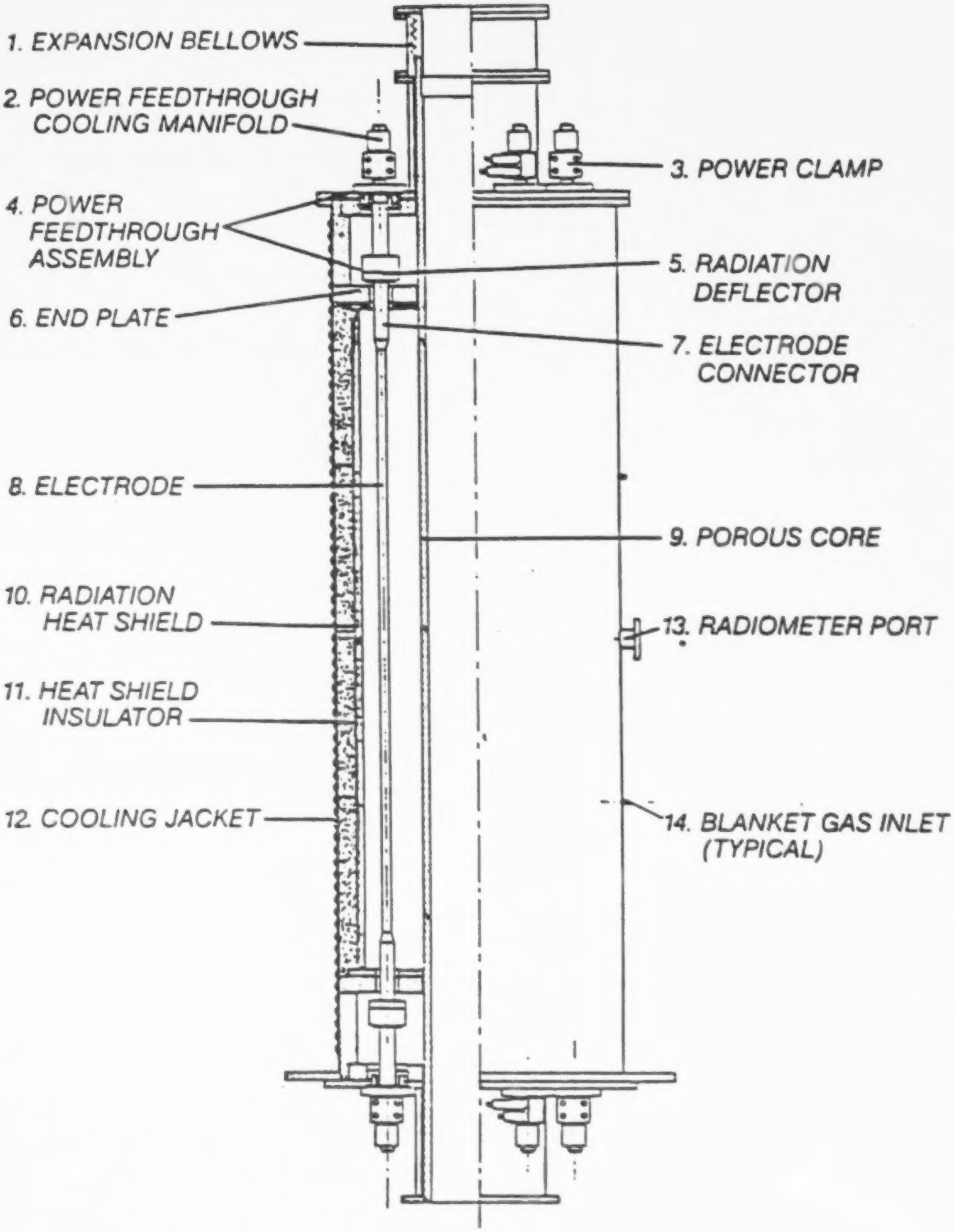


Figure 11.4.3. Advanced Electric Reactor [Huber].

heated core then radiates heat to the waste materials. The reactor core is isolated from the waste by a blanket of gas formed by nitrogen flowing radially through the porous core walls.

The only feed streams to the reactor are the waste material and the inert nitrogen gas blanket. Therefore, the destruction is by pyrolysis rather than oxidation. Because of the low gas flow rate and the absence of oxygen, long gas phase residence times can be employed, and intensive downstream cleanup of off gases can be achieved economically.

Destruction via pyrolysis instead of oxidation significantly reduces the concentrations of typical incineration products such as carbon dioxide and oxides of nitrogen. The principal products formed during treatment of halogenated solvents would be hydrogen, chlorine (if calcium oxide is added to the reactor, calcium chloride is formed instead), hydrochloric acid, elemental carbon, and free-flowing granular material.[18-20]

A process flow diagram for the AER is shown in Figure 11.4.4. The waste, if it is a solid, is released from an air tight feed bin through a metered screw feeder into the top of the reactor. If it is a liquid, it is fed by an atomizing nozzle into the top of the reactor. The waste then passes through the reactor where pyrolysis occurs at temperatures of approximately 4500°F (2480°C) in the presence of nitrogen gas. Downstream of the reactor, the product gas and waste solids pass through two post-reactor treatment zones, the first of which is an insulated vessel which provides additional high temperature (2000°F or 1090°C) and residence time (5 seconds). The second post-reactor treatment zone is water-cooled, and its primary purpose is to cool the gas prior to downstream particulate cleanup.

Off gas cleaning equipment includes a cyclone to collect particles which do not fall into the solids bin, a bag filter to remove fines, an aqueous caustic scrubber for acid gas and free chlorine removal, and two banks of five parallel activated carbon beds in series for removal of trace residual organics and chlorine.

The stationary pilot scale reactor which has been used for testing various wastes at Huber's Borger, Texas facility consists of a porous graphite tube, 1 foot in diameter and 12 feet high, enclosed in a hollow cylinder with a double wall cooling jacket. This pilot unit is capable of processing 5000 tons/yr of waste. Huber also has a 3 inch diameter mobile unit which has been transported to hazardous waste sites for testing purposes.

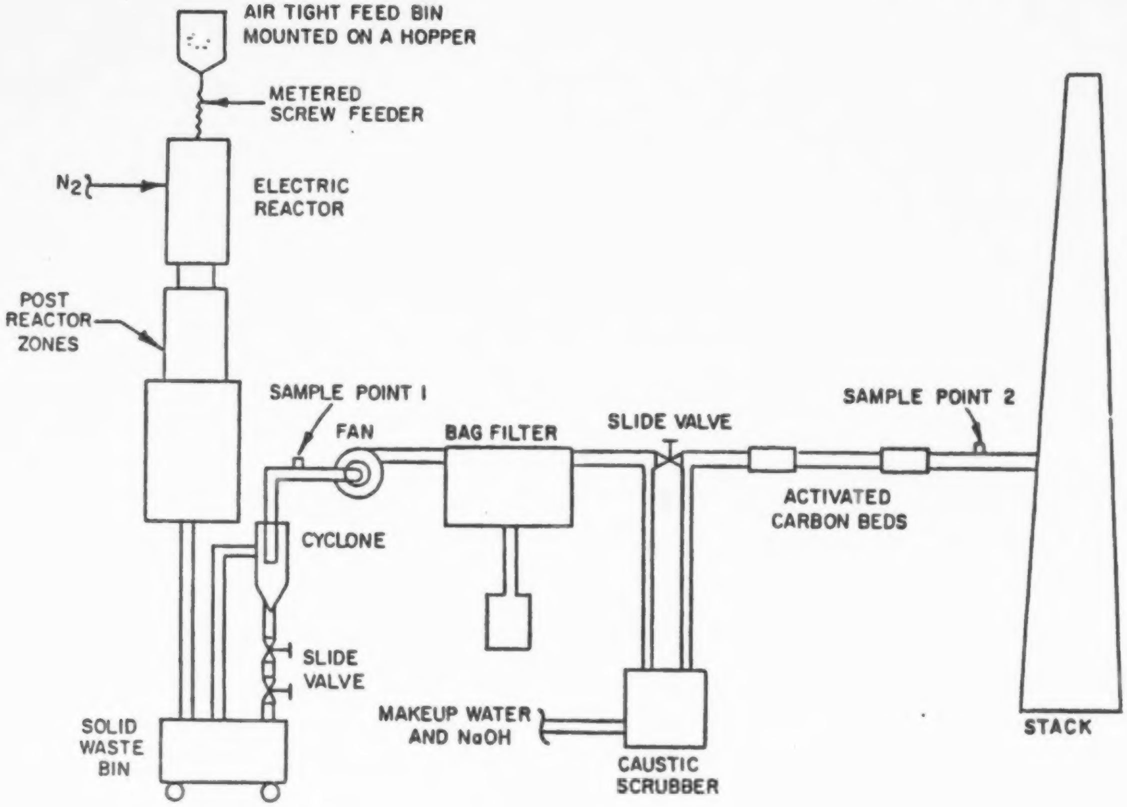


Figure 11.4.4. High temperature fluid wall process configuration for the destruction of carbon tetrachloride [Huber].

The AER cannot currently handle two-phase materials (i.e., sludge); it can only burn single-phase materials consisting of solids, or liquids, or gases alone.[19,21] Generally, a solid feed must be free flowing, nonagglomerating, and smaller than 100 mesh (less than 149 micrometers or 0.0059 inches).[19] However, depending on the required destruction, solids smaller than 10 mesh may be suitable. Soils should be dried and sized before being fed into the reactor.

The Huber process is not cost competitive with standard thermal destruction techniques (such as the rotary kiln) for materials with a high Btu content.[18,21] It is cost-effective for wastes with a low Btu content (e.g., chlorinated solvents) because unlike standard thermal destruction techniques, the Huber process does not require supplementary fuels to obtain the necessary Btu content for incineration.

The operating parameters as described by References 19 and 21 are as follows:

• Residence Time (100 mesh solids)	0.1 seconds
• Gas Flow Rate	500 scfm for 150 ton/day
• Gas Phase Residence Time (at 2500°F or 1370°C)	5 seconds

11.4.3.2 Demonstrated Performance--

In 1983, Thagard conducted a series of tests on PCB-contaminated soils using a 3-inch diameter research reactor.[22] The results of these tests showed an average DRE of 99.9997 percent. The destruction efficiency was found to be independent of the feed rate in the 50 to 100 g/m range at 2343°C. Pyrolysis products other than carbon and hydrogen chloride were not detected using a GC with electron capture detection. It was concluded that the method for dispersing the feed into the reactor needed improvement. Problems with slagging in the reactor occurred that were believed to be related to the small diameter of the reactor and also to the design of the fluid wall flow. After modifications, additional tests on a 6-inch prototype reactor were conducted by Thagard using hexachlorobenzene dispersed on carbon particles; 99.99991 percent destruction efficiency was achieved.[22]

J. M. Huber Corporation purchased the patent rights and made further improvements to the process.[21] The J.M. Huber Corporation then began tests in its stationary reactor system which has a diameter of 12 inches. Included in this system are: an insulated post-reactor vessel, a water-jacketed cooling vessel, a cyclone, a baghouse, a wet scrubber, and an activated carbon bed. Several research burns have been conducted with this system. Results and operating parameters for pertinent burns are summarized in Table 11.4.2.

A series of four trial PCB-burns were conducted during September 1983 using a synthesized mixture of Aroclor 1260 and locally available sand to obtain a total concentration of 3000 ppm PCBs.[1,19] After treatment, the sand had a PCB content ranging from 0.0001 to 0.0005 ppm (0.1 to 0.5 ppb). The destruction and removal efficiency was measured to be 99.99960 to 99.99995 percent. Additional studies were conducted with the 12 inch diameter reactor using soils contaminated with octachlorodibenzo-p-dioxin (OCDD) and carbon tetrachloride. Seven nines DRE (99.99999 percent) were reportedly achieved at feed rates up to 2500 lbs/hr.

11.4.3.3 Cost of Treatment--

Operating costs will vary depending on the quantity of material to be processed and the characteristics of the waste feed. Pretreatment may be necessary for bulky wastes having a high moisture content. Typical energy requirements for contaminated soils range from 800 to 1000 kwh/ton.

Cost estimates for processing contaminated soil at a site containing more than 100,000 tons of waste material were approximately $365 to $565/ton in 1985. The cost breakdown for this estimate was 12 percent for maintenance, 7 percent labor, 29 percent energy, 18 percent depreciation and 34 percent for other costs (permitting, setup, post-treatment, etc.).[24,25] These costs have recently been updated. The new costs are expected to be released in 1986.[21]

11.4.3.4 Status of Technology--

Huber maintains two fully equipped reactors at their pilot facility in Borger, Texas (Schofield,[19] et al., 1985). The smaller reactor, which is equipped for mobile operation, has a 3-inch core diameter and a capacity of 0.5 lb/min.. The larger reactor is commercial scale with a 12-inch core

TABLE 11.4.2. SUMMARY OF OPERATING PARAMETERS AND RESULTS FOR HUBER AER RESEARCH/TRIAL BURNS

Condition	PCBs (Sept. 1983)	CCl4 (May 1984)	Dioxins (Oct/Nov 1984)
Reactor Core Temperature (°F)	4100	3746-4418	3500-4000
Waste Feed Rate (lb/min)	15.5-15.8	1.1-40.8	0.4-0.6
Nitrogen Feed Rate (scfm)	147.2	104.3-190.0	6-10
%-DRE	99.99999	99.9999	99.999

Source: References 19 and 23.

diameter and a capacity of 50 lb/min. Both of these reactors are used primarily for research purposes. In May 1984, the Huber reactor was certified by the EPA under TSCA to burn PCBs wastes. Recently, the U.S. EPA and the Texas Water Commission jointly issued J.M. Huber Corporation a RCRA permit which authorizes the incineration of any non-nuclear RCRA hazardous waste (including dioxin-containing wastes) in the Huber Advanced Electric Reactor.[26] This was the first commercial permit issued under RCRA for treating dioxin-containing wastes. The J.M. Huber Corporation intends to use the permit for research and development of a full-scale transportable AER. Huber does not intend to operate a hazardous waste disposal operation, but rather to construct and market stationary and/or mobile units for use by companies or organizations involved in hazardous waste destruction.[21]

11.5 IN SITU VITRIFICATION

In situ vitrification (ISV) was originally developed by Battelle Pacific Northwest Laboratories as a means of stabilizing in-place high level nuclear waste. More recently, however, ISV has been studied as a means of destroying soils contaminated with chlorinated organic wastes, including PCBs and dioxin wastes, and heavy metals. The system was patented in 1983.

In situ vitrification converts contaminated soils, or sludges, into a solid glassy matrix through melting by joule heating. As depicted in Figure 11.5.1, the process begins when graphite electrodes are placed into the ground in a square array. A conductive path is established by placing graphite over the soil between the electrodes. Electrical current is passed between the electrodes, creating high temperatures (1,700°C or 3,100°F) which melt the soil, and pyrolyze the organic waste constituents. Gaseous effluents which are produced are collected by a hood over the area and are exhausted to off-gas treatment systems. When pyrolysis is complete, current is shut off and the mass cools to form a glass like material. A picture of the system is presented in Figure 11.5.2, showing the enclosed hood.

Battelle engineers have developed 30 kw, 500 kw, and 3750 kw size units. The small unit produces up to a ton of vitrified mass per setting, the 500 kw unit produces approximately 10 tons per setting, and the large unit produces 400 to 800 tons per setting.)

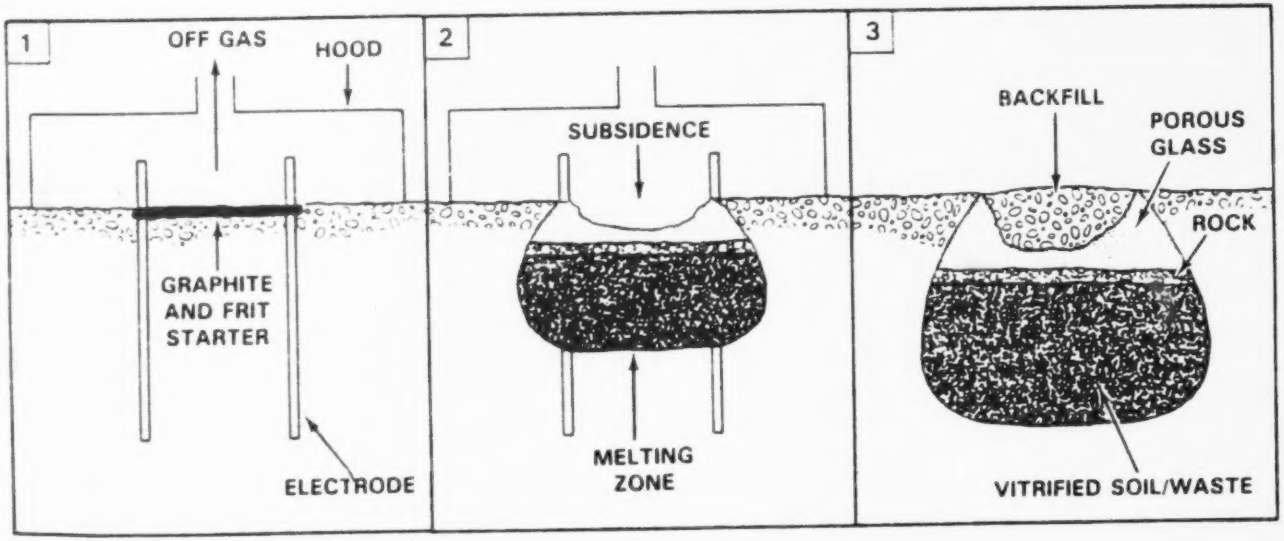


Figure 11.5.1. Operating sequence of in situ vitrification.

Source: Reference 27.

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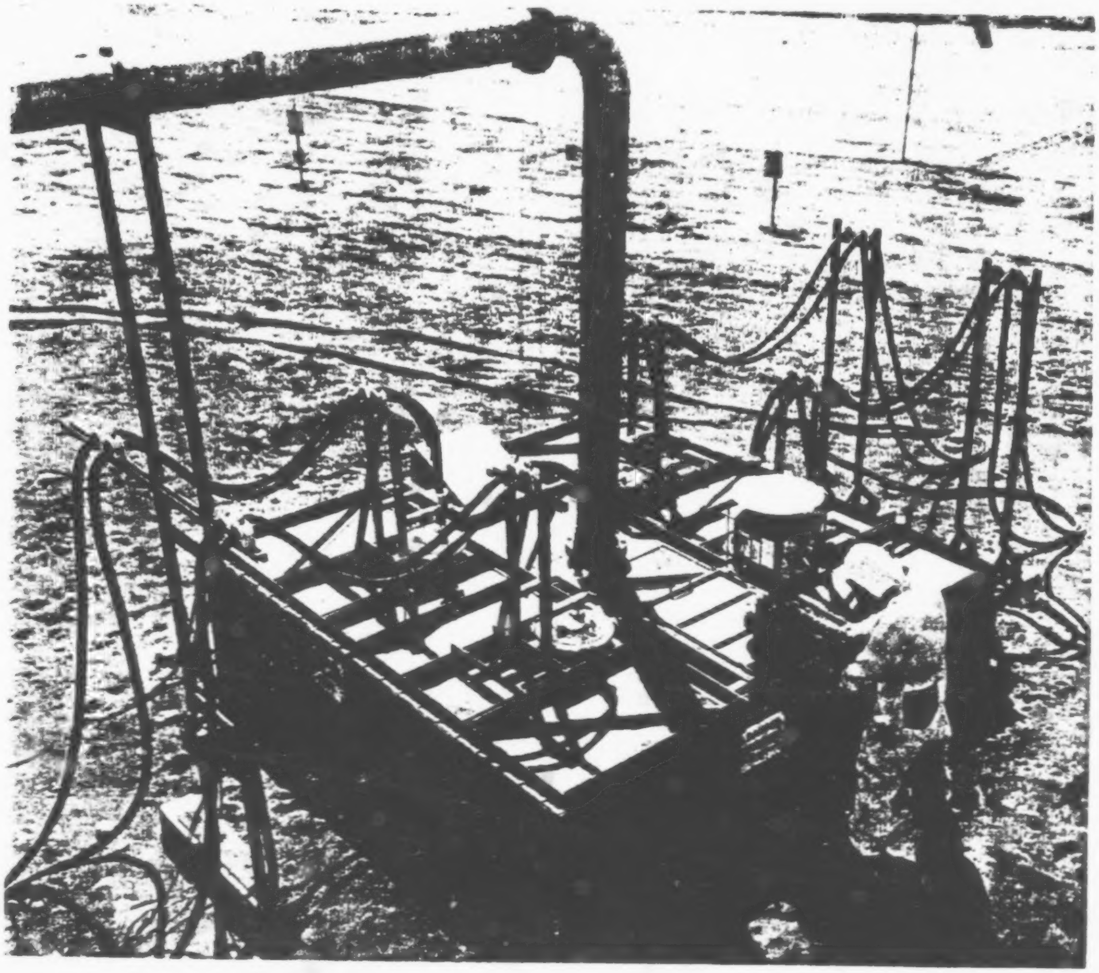

Figure 11.5.2. Off-gas containment and electrode support hood.

Source: Reference 27.

The cost estimates reported by PNL, and discussed below for TRU wastes treated by the ISV process, account for charges associated with site preparation, consumable supplies such as electrical power, and operational costs such as labor and annual equipment charges.[28] Specifically, for variations in manpower levels, power source costs, and degree of heat loss, it was determined that the costs for TRU waste vitrification ranges from 160 to 360 $\$/m^3$ to vitrify to a depth of 5 meters. These costs are a function of many variables, but are most sensitive to variations in the amount of moisture in the soil and the cost of electrical power in the vicinity of the process. Figure 11.5.3, developed by PNL, illustrates the variation in total costs as a function of both electrical power costs and the moisture content of TRU soil experimentally treated. The vertical line represents the value beyond which it is more cost effective to lease a portable generator.

Recently, PNL has assessed the cost implications for ISV treatment of three additional waste categories; i.e., industrial sludges and hazardous waste (PCB) contaminated soils at both high and low moisture contents.[30] Representatives at PNL indicated that for industrial sludges with moisture contents of 55 to 75 percent (classified as a slurry), the total costs would range from 70 to 130 $\$/m^3$. Additionally, treatment of high (greater than 25 percent) moisture content hazardous waste-PCB contaminated soil would cost approximately 150 to 250 $\$/m^3$ versus costs of 128 to 230 $\$/m^3$ for low (approximately 5 percent) moisture content PCB contaminated soil.

As these recent data and past TRU waste cost data suggest, the moisture content of the contaminated material treated is particularly important in influencing treatment costs; high moisture content increases both the energy and length of time required to treat the contaminated material. Furthermore, PNL representatives suggest that treatment costs are also influenced by the degree of off-gas treatment required for a given contaminated material, i.e., ISV application to hazardous chemical wastes will likely not require as sophisticated an off-gas treatment system as would TRU waste treatment.

PNL has recently assessed the treatment of and costs associated with hazardous waste contaminated soils. Specifically, during the summer of 1985, tests were conducted for the Electric Power Research Institute (EPRI) on PCB

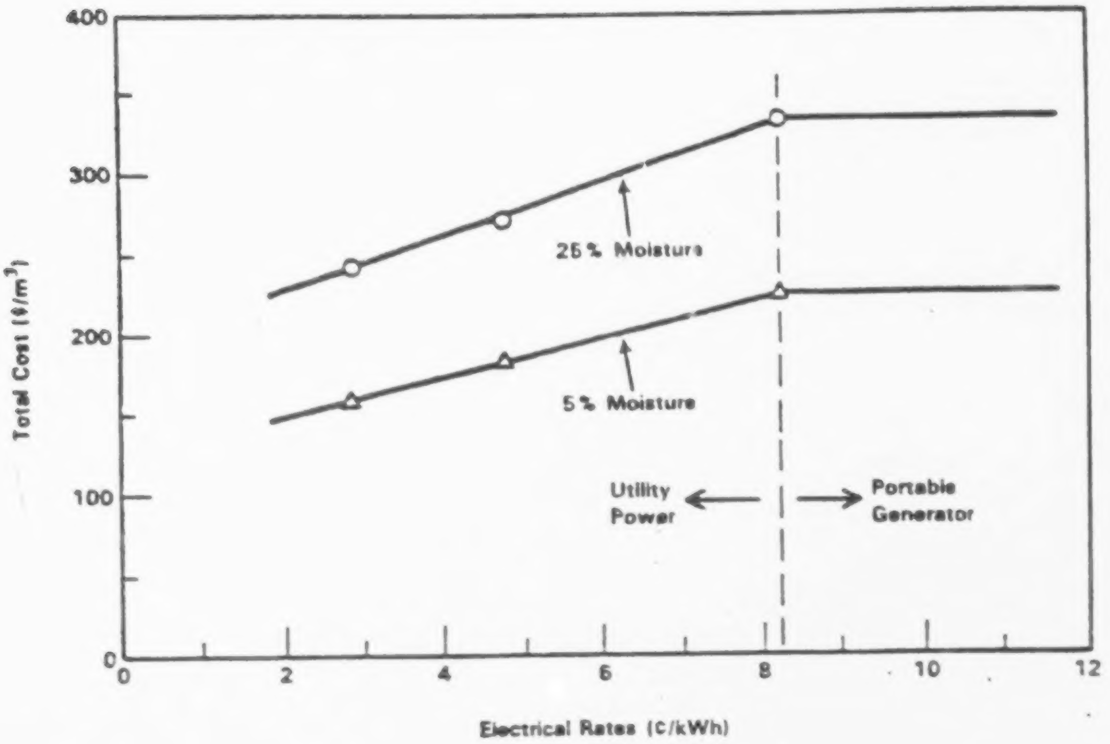

Figure 11.5.3. Cost of in situ vitrification for TRU wastes as functions of electrical rates and soil moisture [Fitzpatrick, 1984].

contaminated soil. While the draft report on these tests has been completed, it has not been published and/or made available to date. However, an EPRI project summary publication, dated March 1986, entitled "Proceedings: 1985 EPRI PCB Seminar" (EPRI CS/EA/EL 4480) has recently been made available to EPRI members. Preliminary results suggest that a destruction/removal efficiency (DRE) of six to nine nines was achieved from the off-gas treatment system overall, and that a vitrification depth of 2 feet was achieved. Additional information will soon be available to the public. PNL expects to continue with research in the area of hazardous waste soils.

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SECTION 12.0

USE AS A FUEL

Numerous studies have been conducted to identify existing industrial combustion processes which have the capability of destroying hazardous wastes through use as a fuel. If hazardous wastes can be used, either in conjunction with, or instead of, the primary fossil fuels currently used, this would provide a dual cost benefit of both eliminating the cost of disposal and lowering consumption of expensive, potentially unavailable sources of energy.

The general guidelines established for identifying suitable high temperature industrial processes (HTIPs) are that they should be capable of achieving levels of performance which are consistent with the requirement established for hazardous waste incinerators; these requirements (as specified in the Federal Register 1982, 47, 27516-35) are:

- at least 99.99% destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in the waste feed;
- at least 99% removal of hydrogen chloride from the exhaust gas if hydrogen chloride stack emissions are greater than 4 lb/h; and
- particulate emissions not exceeding 0.08 grains/dry standard cubic foot (dscf), corrected to 7% oxygen in the stack gas.

PEDCo[1] has identified over 100 HTIPs which are capable of operating at temperatures exceeding 1200°F in the metallurgical, chemical, mineral, and sewage sludge processing industries. Of that number[1], 15 separate technologies are considered to be prime candidates for thermal destruction of hazardous wastes, based on preliminary test programs. These technologies are listed in Table 12.1.

Performance testing has demonstrated the ability of several HTIPs to achieve effective levels of hazardous waste destruction. The studies have also indicated, however, that the applicability of most HTIPs to hazardous

TABLE 12.1. THERMAL TECHNOLOGIES CONSIDERED APPROPRIATE FOR BURNING HAZARDOUS WASTE AS FUEL

Process or reactor	Industry	Exit and maximum temperature °C	Average residence time (secs)
Tunnel Kiln	Brick	260 - 1,180	4.3
Oil Furnace	Carbon Black	870 - 1,400	1.1
Reverberatory Furnace	Primary Copper	1,300 - 1,400	2.2
Blast Furnace	Primary Lead	700 - 1,200	5.9
Multiple Hearth Roaster	Primary Zinc	200 - 980	>10
Suspension Roaster		930 - 1,010	>10
Fluidized-Bed Roaster		950 - 1,740	>10
Blast Furnace	Iron & Steel	1,100 - 1,870	1.1
Open Hearth Furnace		1,200 - 1,800	2.0
Long Rotary Kiln	Lime	680 - 1,900	8.3
Short Rotary Kiln/Preheater		1,160 - 1,840	7.6
Rotary Kiln	Aggregate	370 - 1,150	3.6
Melting Furnace	Glass	620 - 1,480	4.1
Fluidized-Bed Furnace	Sewage Sludge	760 - 870	1.4
Multiple-Hearth Furnace		480 - 980	0.5

Source: Reference 1.

waste destruction is limited by many factors. Primarily, these limitations include the negative impact of hazardous waste combustion byproducts on HTIP equipment and their potential environmental impact. Not all HTIPs will be adequately equipped with air pollution controls, other effluent (liquid and solid waste) controls, and material transport systems needed for hazardous waste combustion. The applicability of wastes exhibiting certain characteristics to usage as a fuel is, therefore, limited in some cases. These primary restrictive characteristics include high water, chlorine, and metal/inorganic content, and high liquid viscosity.

Of the various high temperature industrial processes studied, three technologies have demonstrated particular promise in achieving adequate levels of performance for a variety of wastes and have, therefore, received the most attention to date. These include: industrial boilers; industrial rotary kilns including aggregate (cement, asphalt) processing kilns and lime processing kilns; and blast furnaces. These units are generally applicable for the combustion of many of the organic solvents and other low molecular weight organic compounds considered in this document. According to Reference 2 approximately 380 million gallons/year are burned as supplemental boiler fuels. The characteristics of many of the solvent hazardous wastes are such that usage as a fuel is considered a technically feasible and economically attractive management alternative. Those characteristics which contribute to the use of solvent hazardous wastes as a fuel include their significant energy content, as indicated in Table 12.2, the fact that many of the solvents may be pumped and atomized in liquid injection burners, and their ability to blend with a wide variety of fuels and other wastes. Most solvent wastes, in fact, will sustain combustion without the use of auxiliary fuel.

Solvent hazardous wastes do exhibit, however, certain characteristics which limit their application to specific high temperature industrial process technologies. The high temperature industrial processes in which hazardous wastes may be burned as a fuel are, in general, more limited in the types of waste streams they can handle effectively than are hazardous waste incinerators. Generally, they are not equipped with extensive air pollution controls or ash recovery and handling systems. Other technical limitations to burning hazardous wastes in HTIPs include:

TABLE 12.2. REPRESENTATIVE HEATING VALUES OF VIRGIN AND SPENT SOLVENTS

Solvent classification	Range @ 0% solids	Typical heating value* (Btu/lb)				
		0% solids	5% solids	10% solids	15% solids	20% solids
Aliphatics	20,000 - 22,000	21,000	19,950	18,900	17,850	16,800
Aromatics	17,000 - 19,000	18,000	17,100	16,200	15,300	14,400
Esters	9,000 - 15,000	12,000	11,400	10,800	10,200	9,600
Ketones	12,000 - 15,000	13,000	12,350	11,700	11,050	10,400
Ethers	12,000 - 15,000	13,000	12,350	11,700	11,050	10,400
Halogenated	500 - 8,000	5,000	4,750	4,500	4,250	4,000
Alcohols	8,000 - 16,000	12,000	11,400	10,800	10,200	9,600

*Assumes zero heating value of solid material in spent solvent; contaminants such as greases could add to values shown.

Source: The Pace Company, Reference 2.

- Possibly more frequent shutdown for boiler cleaning due to fouling of the boiler tubes;
- High flue gas exit temperatures needed to prevent condensation of acidic components; and
- Safety problems associated with low boiling point/ignitable solvents.

In general, the assessment of the potential for a specific waste to be destroyed by using it as a fuel in a specific system is based on identification of certain key characteristics. These characteristics may be classified as follows:

- Those which restrict the ability of a system to effectively distribute the waste within the combustion zone;
- Those which limit the ignitability and continuous combustibility of a waste;
- Those which promote the generation of gaseous emissions and/or liquid and solid effluent streams which are difficult to manage; and
- Those which affect the overall quality of the product.

The primary characteristics to be identified in this regard are summarized below:

- Physical Form--The physical form of a waste dictates the manner in which it may be input to the system, and the relative ease with which it will burn.
- Btu (Heat) Content--Wastes must exhibit high heats of combustion to be considered as a fuel. A common standard used to determine whether a waste may sustain combustion adequately for this purpose is 8,500 Btu/lb, thus a waste with a Btu value below 8,500 probably cannot be used as a fuel without blending.
- Chlorine Content--Chlorine presents a limitation to the process both due to the general low combustibility of highly chlorinated substances and due to the composition of byproducts of combustion. Most HTIPs are not equipped with air pollution controls which can adequately handle acid gases produced when chlorinated wastes burn, nor can they withstand the corrosive attack of hydrochloric acid on linings and internal surfaces. A chlorine content of 3 percent is considered a maximum.

- Metals/Ash/Organic Salt Content--Wastes which contain high levels of solid, thermally inert materials are not generally good candidates for usage as a fuel, due to their negative environmental impact (particulate emissions), and possible impact on the quality of the products. Solids in the fuel feed also tend to have a deleterious effect upon HTIP equipment, for example, fouling of boiler tubes.
- Water Content--Water is a hindrance to effective combustion, and may also affect product quality. High moisture content wastes, therefore, are generally not good candidates for combustion as a fuel.
- Flash Point--Safety considerations require that highly ignitable components be removed prior to their storage and introduction into combustion systems.

The specific characteristics of wastes which present restrictions to the applicability of the technologies focused upon in this document will be discussed in the next section.

12.1 PROCESS DESCRIPTIONS

12.1.1 Industrial Boilers

Boilers are used primarily to produce steam, for use in processing or space heating. The population of industrial boilers in service may number over 300,000 in the United States,[3] and consists of many different types of systems, available in sizes ranging from several thousand to several hundred million Btu/hour, utilizing a wide variety of fuels, mechanisms for fuel feed, and heat transfer systems.

Two types of boilers are considered appropriate for the burning of hazardous wastes: water tube and fire tube boilers. These systems are considered appropriate because combustion of wastes and production of combustion byproducts are physically separate from the heat transport media, thus preventing cross-contamination of the media and allowing for greater control of the combustion process. Both water tube (WT) and fire tube (FT) boilers employ a "shell-and-tube" arrangement. In a water tube boiler, wastes are burned within a combustion zone through which tubes containing flowing water (or steam) are passed. Hot combustion gases contact the outer (metal) walls of the tubes, imparting thermal energy which is transferred to the water flowing inside. High pressure, high temperature steam is thus produced within the tubes. WT boilers are most commonly found in the 10 mm Btu/hour or larger range.[4] They are capable of burning any physical form of fuel, and are consequently applicable to a wide variety of waste types.

Fire tube boilers employ essentially the opposite configuration to water tube boilers. Fuel combusting within the tubes produces thermal energy which heats water through which the tubes are passed. FT boilers employ liquid fuels only, and are generally available in smaller sizes.[4] FT boilers may be more subject to structural failures when large variations in operation or fuel feed occurs.[5]

Both water tube and fire tube boilers are usually capable of achieving combustion temperatures and residence times which are sufficiently long to achieve high levels of waste destruction. When used as a fuel in a boiler, wastes are typically blended with conventional fuels to achieve a final waste/fuel mixture which has a heat content above some specified level. Waste/fuel mixture ratios vary widely, from as low as 5 to 10 percent by weight to 100 percent waste.[6] The waste/fuel ratio selected depends upon the suitability of the waste for use as a fuel, as determined by several factors. These factors include the compatibility with fuel handling and burner/boiler systems, physical form of the waste, heat content, moisture content, concentration of sulfur, halogens, metals, and other noncombustible materials, and liquid viscosity. Many boilers burning wastes with fuels have established certain baseline limitations relative to these factors. For example, the maximum acceptable chlorine content for boilers is typically set at 3 percent by weight.[7] Typical pretreatment methods in addition to blending to achieve heat content requirements are operations such as sedimentation, screening and other separation techniques to reduce water and sediment and to eliminate, if necessary light ends which represent a storage and combustion hazard.

Blending of hazardous solvent wastes with conventional fuel oils can also serve the major purpose of meeting regulatory emission requirements, thus avoiding the need to install costly air pollution control devices. Boilers firing conventional fuels rarely employ air pollution controls because combustion efficiencies are high and the ash content (<0.1 percent) and chlorine content (<0.01 percent) of the fuels are low. Thus, uncontrolled particulate and hydrochloric acid emissions are low and generally below any applicable regulatory limits. Although the regulatory requirement for incinerators are stringent, blending with conventional fuels appears to be a viable means of meeting these regulatory requirements for some wastes. Assuming that ash is the sole source of particulate emissions, the regulatory requirement that particulate emissions can not exceed 0.08 grains/dry standard cubic foot, corrected to 7 percent oxygen in the flue gas, can be met by a fuel containing about 0.28 percent ash. This estimate assumes that ash is the sole source of particulate emission, that all ash is emitted, the BTU content of the fuel is 19,000 BTU/lb, and that the chemical composition of the fuel is similar to that of a number 6 fuel. This level of particulate emissions is equivalent to an emission factor of 67 nanograms per Joule, a value somewhat higher than EPA emission factors of 37 and 6 nanograms per Joule for uncontrolled boilers burning residual and distillate oil, respectively. While the above estimate is only approximate, it shows that blending may be a viable option for some wastes. For example, a 10 percent blend of a one percent ash content waste with distillate oil would probably meet particulate emission requirements, and even higher blending levels may be possible.

Similary, most nonhalogenated wastes could meet the incinerator chlorine emission level of 4 lb/h. For example, a 10,000,000 BTU/h boiler could burn a 0.4 percent chlorine content, 10,000 BTU/lb fuel and meet the regulatory requirement. However, a one percent blend of 1,1,1 Trichloroethane (100 percent) with a 19,000 BTU/lb fuel oil would exceed the 0.4lb/h emission level. Halogenated solvents, because of both low BTU content and high chlorine levels, are not suitable for use as boiler fuels. However, they can be destroyed in controlled incinerators and can, as noted below, be burned in certain industrial processes where the HCl emissions are adsorbed and/or provide a process benefit.

12.1.2 Industrial Kilns

There are several industrial processes which employ rotary kiln units that are similar to units whose hazardous waste destruction capabilities have been studied in depth. These industrial kilns include those used in the aggregate processing (cement and asphalt) and lime industries. The interest in these systems is based upon two major factors. First, they operate at temperature ranges and residence times required for effective destruction of hazardous waste constituents. Second, they provide a large and widely distributed source of capacity; thus reducing transportation costs and materials handling considerations.

Another possible advantage to be gained from the use of wastes cofired as fuels in industrial kilns relates to the benefits to be realized from the firing of halogenated compounds. As noted in Section 4, cement kiln can use up to 1.25 percent of their design feed as chlorine waste.[2] Blast furnaces are also reportedly burning chlorine containing wastes to prevent build up of alkalis on furnace walls.

A brief overview of prime candidate industrial kiln systems is presented below.

Lime Kilns--

Lime production processes use high temperature kilns to produce CaO ("quicklime") from limestone ($CaCO_3$). A number of different thermal process designs are used in lime production, with rotary kilns accounting for approximately 90 percent of production capacity.[1] According to the U.S. Bureau of Mines, 153 lime plants were in operation in 1980.[1]

The process involved in lime production is relatively simple. Limestone is fed to the elevated end of the kiln and is discharged as quicklime at the lower end. Combustion air flows upward, countercurrent to the lime, and is exhausted to air pollution controls (dust collectors such as ESPs or baghouses) at the feed end of the kiln. Most kilns, according to PEDCo, are fired with pulverized coal, but also can fire natural gas and oil. Adaptability to both solid and liquid hazardous wastes, therefore, is excellent.

The potential effectiveness of the lime kiln in destroying hazardous wastes used as fuel is considered high. This is primarily due to the high temperatures (~2300°F) of operation. However, waste composition is important since impurities introduced into the feed such as alumina, silica, and iron in the waste may lead to formation of undesirable inorganic salts and affect the utility of the product. For example, chlorine in the waste may react to form calcium chloride, the formation of which may lead to not only fouling of the product, but also to clogging of the kiln when temperatures go below 1400°F. HCl formation may also lead to corrosion in ducts and in the air pollution control equipment (baghouses, for example, may not be able to handle corrosive gases).

Aggregate Kilns

Aggregate kilns are used to produce mixtures such as cement and asphalt. Typical raw materials used to produce cement or asphalt include:

- Natural lightweight aggregates - prepared by crushing and sizing pumice, volcanic cinders, tuff, scoria, and breccia;
- Byproduct lightweight aggregates - prepared by crushing and sizing foamed and granulated slag (e.g., from blast furnace operations in the iron and steel industry), coke breeze, and cinders; and
- Manufactured structural lightweight aggregates - prepared by pyro-processing clay, shale, or slate.[1]

The process involved in aggregate processing is very similar to that used in lime manufacturing. Dry raw materials are reacted within a kiln whose operating temperature falls between 2050 and 2300°F[8]. Typical residence times are 2 to 4 seconds. Excess air usage is high, usually exceeding 100 percent.[1,9] The temperatures and residence times of the processes are high enough to ensure adequate levels of destruction. Unlike lime, aggregate quality is not as significantly impacted by hazardous waste combustion byproducts. Thus, sorption of certain byproducts within the aggregate can be tolerated. Burning of hazardous wastes in aggregate kilns appears to be limited primarily by the effect combustion byproducts will have on the kiln and on air pollution control requirements.

Hazardous waste containing fuels have been used by Systech Corporation of Xenia, Ohio in their cement kiln operation.[9] Their specifications restrict the chlorine content of waste to less than 3 percent by weight metal content (lead, barium, zinc, and chromium) to less than 4,000 ppm, and ash content to less than 7 percent. A Btu content of no less than 10,000 Btu/lb is also specified. Specifications are shown in Table 12.3. Other information compiled by Radian Corporation setting water property restrictions for aggregate kilns is very similar (see Table 12.4).[10]

TABLE 12.3. OPERATING SPECIFICATIONS; SYSTECH CEMENT KILN PROCESS

Parameter	Waste category 1	Waste category 2	Waste category 3
Applicability	Will be accepted 100 percent of the time	Accepted with some blending at the facility	Blending is required before shipment
Heat content	10,000 Btu/lb, minimum	8,500 - 10,000 Btu/lb	6,000* - 8,500 Btu/lb
Viscosity	<100 cp	100 - 200 cp	200 - 330** cp
Chloride content	< 3 percent, by weight	3 - 5 percent	5 - 10 percent
Metals (lead, barium, zinc, chromium)	< 4,000 ppm each	4,000 - 6,000 ppm each	6,000 - 10,000 ppm each
Ash content	<7 percent	7 - 10 percent	10 - 15 percent
Water (separated)	<7 percent	1 - 2 percent	2 - 3 percent

*Material under 8,500 Btu/lb must have less than 5 percent chlorine.

**Limit to pumpability.

Source: Systech Corporation, 1986 (Reference 9).

TABLE 12.4. OPERATING SPECIFICATIONS OF COMMERCIAL AGGREGATE KILNS BURNING WASTES

Parameter	Facility[1]	Facility[2]
Heat content	Must be ≥80,000 Btu/gal (high enough to sustain combustion).	≥90,000 Btu/gal
Halogen content	<5 percent, by weight, chlorine may damage resin refractory and scrubber due to corrosivity. Blending is done to wastes >3 percent chlorine.	< 3%
Viscosity	200 cp	
Suspended solids	<10 percent, by weight, must pass through a 1/8 inch screen.	
Metals content	Cannot exceed state emission regulations.	
Ash content	<8 percent	< 5%
Sulfur content	<2.5 percent	
Water content	No separated streams	< 10%
Physical form	Liquids and sludges only. No solids.	

Source: Reference 10.

12.2 DEMONSTRATED PERFORMANCE

The performance of industrial boilers and other high temperature industrial processes, firing solvents and other low molecular weight organics, as measured by emissions, can be considered comparable in many cases to that shown by hazardous waste incineration technologies. This is true even though environmental regulations do not currently require equivalent performance. The high level of performance of the conventional fuel burning systems is attributable to the high temperatures and long residence times achieved in the combustors without regard to their potential use as hazardous waste combustors.

Air emissions, contaminated scrubber liquors and sludges, and combustion ash generated during the combustion of hazardous wastes in HTIPs can pose significant problems. Clearly, the significance of certain pollutants is attributable to both process design and waste characteristics. The determination of the actual environmental impacts associated with the combustion of any specific waste in a specific system will have to be assessed on a case-by-case basis.

Numerous studies of the effectiveness of hazardous waste fuel burning technologies have been conducted. In this section, a number of the performance tests conducted, primarily those carried out under sponsorship of the U.S. EPA, will be discussed, and key factors influencing performance will be examined.

12.2.1 Industrial Boiler Tests

The performance of industrial boilers burning hazardous wastes has been studied extensively. The primary body of information on this technological alternative was provided in a U.S. EPA sponsored study conducted by Acurex Corporation in 1984.[5] This study and others have indicated that industrial boilers are capable of achieving high levels of performance as measured by hazardous waste destruction (DREs of more than 99.99 percent) with suitable waste feeds. These results are attributed to the fact that the boilers have high combustion temperature capability and long residence times. However, even for these units, emissions of particulate matter and hydrogen chloride can be excessive for high ash and chlorine fuel blends burned in boilers which are not equipped with appropriate emissions control devices.

Investigation of site-specific test data has revealed certain possible trends in DREs, emissions and PIC formation. The results of several boiler studies are described in more detail below.

Acurex Corporation, 1984[5]--

In the most comprehensive study conducted to date on hazardous waste destruction in industrial boilers, Acurex Corporation evaluated the performance of 11 different industrial boilers cofired with hazardous wastes. Boilers were tested for destruction and removal efficiency (DRE), emission of particulate matter, acid gas and organics, and formation of products of incomplete combustion (PICs). A variety of wastes streams, all of which contained hazardous solvents or ignitables, were cofired in these boilers, as described in detail in Reference 5 and shown in Table 12.5. In summary, wastes streams fired contained a variety of low molecular weight organic compounds (POHCs) in wastes, representing wide ranges in chlorine content, moisture content, and ash content. Operation of the boilers with "typical" industrial conditions of heat input, waste/fuel ratio, and excess air was attempted.

As summarized in Table 12.6, the DREs achieved during this test program were at a uniformly high level, including those for the chlorinated solvents that are generally considers difficult to destruct. Average DREs for carbon tetrachloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, benzene, toluene, tetrachloroethylene, and methyl methacrylate exceeded 99.99 percent DRE. DREs for carbon tetrachloride were generally lower than those measured for other POHCs, but were generally greater than the standard of 99.99 percent.

The test results were interpreted to indicate that DREs achievable by industrial boilers are limited primarily by "nonsteady" boiler operation including fluctuating waste feed rates and varying excess air levels present in the combustion zone. Such conditions are often characterized by unstable combustion (fluctuating combustion zone temperatures), high particulate emissions, and soot formation. Carbon monoxide levels were identified as a means of monitoring of boiler operation. Lower DREs were noted when CO levels exceeded 80 to 100 ppm in stack effluent.

TABLE 12.5 BOILER SUMMARY

Site	Boiler type	Primary fuel(s)	Waste description	Emission control device	Operational conditions
A	Keeler CP 308-hp (10,000 lb/hr of steam) watertube boiler	Wood waste: chips, bark and sawdust	4 cofire tests - Creosote sludge containing chlorinated aromatics including pentachlorophenol, phenol, naphthalene, and fluorene	Multiclone for particulate collection	Typical wood boiler operation with high excess air and high combustible emissions. Baseline fuel contaminated with creosote. Boiler poorly instrumented.
B	Cleaver-Brooks 250-hp (8,400 lb/hr of steam) firetube boiler	1 baseline test natural gas	3 cofire tests - Alkyd waste water with paint resin containing toluene, xylenes, and several acids	None	Low load tests. Several waste feed problems caused by inefficient mixing of waste and plugging of screens. Fluctuations in waste feed flow.
C	Babcock & Wilcox 29-kg/s (230,000 lb/hr of steam) multiburner watertube	1 baseline test natural gas	3 cofire tests - Phenolic waste containing phenol, alkyl-benzenes, and long-chain aromatic and aliphatic hydrocarbons	None	Low boiler load and high excess air. No operational transients.
D	Babcock & Wilcox 11.4-kg/s (90,000 lb/hr of steam) multiburner watertube[a]	1 baseline test no. 6 oil	3 cofire tests - Waste stream no. 1 - Mixture of methanol xylenes and tetrachloroethylene 3 cofire tests - Waste stream no. 2 - Mixture of toluene and bis(2-chloroethyl) ether	None[b]	Burner problems experienced with waste stream no. 1. Waste feed interruption due to filter plugging. No transients with waste stream no. 2.
E	Combustion Engineering 13.9-kg/s (110,000 lb/hr) of steam single burner packaged watertube	1 baseline test no. 6 oil and natural gas	1 cofire test - Waste stream no. 1 - Mixture of methyl methacrylate, and fluxing oils 6 cofire tests - Waste stream no. 2: waste stream no. 1 spiked with - Carbon tetrachloride - Chlorobenzene - Trichloroethylene 1 cofire test - Waste stream no. 3 mixture of toluene and methyl methacrylate	None	Smoke emissions and transients experienced with spiked waste stream no. 1. Generally higher excess air required during cofiring. Smoke generation sensitive to orientation of waste fuel guns and surges in waste flowrates.

(continued)

TABLE 12.5 (continued)

Site	Boiler type	Primary fuel(s)	Waste description	Emission control device	Operational conditions
F	**Babcock & Wilcox 7.6-kg/s (60,000 lb/hr of steam) multiburner watertube**	1 baseline test no. 6 oil	3 cofire tests - Purge thinner containing mixed methyl esters, butyl cellosolve acetate, aromatic hydrocarbons, aliphatic hydrocarbons. Spiked with chlorobenzene trichloroethylene and carbon tetrachloride	None	Improper setting of burners caused several flame-outs independent of waste feed.
G	Johnston modified firetube boiler 5.0 kg/s (40,000 lb/hr of steam or 1,200-hp). Thermal heat recovery oxidizer (THROX)[c]	None Natural gas used only for startup	3 primary firings - Mixture of chlorinated hydrocarbons containing up to 55 percent by weight chlorine. Major components: - Bis(2-chloroisopropyl) ether - Epichlorohydrin Spiked with carbon tetrachloride	Two chloride recovery/ removal water scrubber columns in series	Steady-state operation. No primary fuel burned.
H	Combustion Engineering tangential NSPS coal-fired boiler 3.2 kg/s (250,000 lb/hr) of superheated steam	1 baseline test Pulverized bituminous coal	3 cofire tests - Crude methyl acetate. Spiked with trichloroethane, carbon tetrachloride and chlorobenzene	Cold side electrostatic precipitator	High boiler load with steady state operation. Low waste/coal heat input.
I	Foster Wheeler AG252 forced draft, bent tube boiler 7.8 kg/s (62,000 lb/hr of steam)	1 baseline test staged 1 baseline test unstaged natural gas	1 cofire staged test, 1 cofire unstaged test - Liquid waste containing nitrobenzene, aniline benzene. Spiked with carbon tetrachloride trichloroethylene, chlorobenzene and toluene	None	Nominal load. No significant boiler transients. Damage to waste feed pumps caused several pump replacements.
J	North American 3200X kg/s (200-hp) packaged firetube boiler	None	6 cofire tests with 2 different trichloroethylene concentrations - Carbon tetrachloride, monochlorobenzene, trichloroethylene, and toluene	None	Half and full loads high and normal EA. No significant boiler transients or impacts.

(continued)

TABLE 12.5 (continued)

Site	Boiler type	Primary fuel(s)	Waste description	Emission control device	Operational conditions
K	Combustion Engineering VU-10 balanced draft, watertube boiler 7.6 kg/s (60,000 lb/hr) of steam	1 baseline test no. 6 oil	1 cofire test - Light and heavy oil mixtures Spiked with carbon tetrachloride, trichloroethylene, and chlorobenzene	None	Nominal test load with no significant boiler operational transients.

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[a] Boiler originally coker-coal fired converted to oil burning.

[b] Some particulate collected by existing hopper cavities.

[c] Patented process for heat generation and chemical recovery of highly halogenated hydrocarbons.

TABLE 12.6 SUMMARY OF TEST AVERAGE DRES FOR VOLATILE POHC

POHC	Site B	Site D	Site E	Site F	Site G	Site H	Site I	Site J	Site K	Range	Weighted average
Carbon tetrachloride			99.9990- 99.9998 (99.9996)	99.980 99.9990 (99.995)	99.9950 99.9990 (99.998)	99.970 99.9994 (99.98)	99.9990- 99.9993 (99.9993)	99.997- 99.9998 (99.9990)	99.9998	99.97- 99.9998	99.9992
Trichloroethylene			99.994- 99.9995 (99.998)	99.98 99.998 (99.996)			99.99990- 99.99992 (99.99991)	99.9980 99.99993 (99.9996)	99.99990	99.98- 99.99993	99.9994
1,1,1-Trichloroethane						99.97- 99.9996 (99.994)				99.97- 99.9996	99.994
Chlorobenzene			99.995- 99.99990 (99.998)	99.96- 99.992 (99.98)		99.990- 99.997 (99.992)	99.997- 99.9990 (99.998)	99.8- 99.97 (99.95)	99.99992	99.8 99.99992	99.992
Benzene							99.97- 99.98 (99.97)		99.996	99.97- 99.996	99.990
Toluene	99.991	99.9992- 99.9999- (99.9996)	99.97	99.90- 99.97 (99.95)			99.998	99.9990 99.9997 (99.9990)	99.99996	99.90- 99.99996	99.998
Tetrachloroethylene		99.994- 99.9992 (99.998)								99.994- 99.9992	99.998
Methylmethacrylate			99.95- 99.997 (99.991)							99.95- 99.997	99.991
Mass-weighted average	99.991	99.994- 99.99990 (99.998)	99.95- 99.9990 (99.995)	99.90- 99.9990 (99.98)	99.995- 99.9990 (99.998)	99.97- 99.9996 (99.991)	99.97- 99.99992 (99.998)	99.8- 99.99993 (99.9990)	99.996- 99.99996 (99.9997)	99.8- 99.99996	99.998

Note: Numbers in parentheses represent the site-average DRE for the POHC.

Source: Reference 5.

The relationship between DRE and several other key factors was also examined. These factors included waste fuel POHC concentration, NO_x formation, surface heat release, and PIC formation. Of those factors, correlations between concentration, surface heat release, and PIC formation were noted.

The relationship between concentration of POHCs in the waste feed (fuel) and ultimate DREs was found to be consistent with DRE versus concentration correlations noted for established hazardous waste incineration technologies. DREs decreased when the concentration of POHCs in the waste feed decreased. DREs correlated negatively with PIC formation, thus linking PIC formation more directly with fuel combustion as opposed to POHC destruction.

Surface heat release rates were generally correlated with DREs. DREs of less than 99.99 percent were found to correspond to surface heat release rates of less than 60,000 Btu/hour ft^2. This result indicates that lower boiler heat input loads may be likely to result in lower DREs, and that the temperature dependence of POHC DREs may be more significant than furnace residence time.

The test results associated with Site G may be of particular importance, because it is the only boiler unit tested which is specifically designed to fire hazardous wastes without auxiliary fuel, and is the only boiler which is equipped to control acid gas emissions. The boiler system consists of a fire-tube boiler retrofitted with two scrubber columns in series. The first column is designed to recover halogen, while the second is designed for acid emission control. Liquid wastes are injected into the unit, which is started up by heating with natural gas. Liquid hazardous wastes are fired without auxiliary fuel if heat content is above 6,000 Btu/lb and are fired with natural gas if below 6,000 Btu/lb.

The wastes fed to the boiler during the test program consisted primarily of chlorinated organics, as shown in Table 12.7. Carbon tetrachloride was added to this waste mixture for this test program. The concentration of CCl_4 was reported to be 40-50 x 10^3 ppm by weight. Chloride content of the waste was found to range from 36 to 48 percent.

Destruction and removal efficiencies were calculated for carbon tetrachloride, and several other POHCs found in the waste stream. The calculated DREs for CCl_4, as shown in Table 12.8, ranged from 99.992 to

TABLE 12.7. COMPOSITION OF TYPICAL WASTE FEED - SITE G

Compound	Weight percent
Bis(2-chloroisopropyl)ether	40.7
Propylene chloride	30.7
Epichlorohydrin	17.2
Propylene chlorohydrin	5.4
Trichloropropylene	3.2
Dichloropropylene	1.4
Propionaldehyde	1.4
Heat content	9,250 Btu/lb

TABLE 12.8. SUMMARY OF POHC DREs, PERCENT -- SITE G

POHC	Test 1	Test 2	Test 3	Weighted Average for All Three Tests
Bis(2-chloroisopropyl)ether	99.9999	99.9999	99.9999	99.9999
1-Chloro-2-propanol	99.9999	99.9999	99.9999	99.9999
t-1,3-Dichloropropylene	99.9999	99.9999	99.9999	99.9999
Epichlorohydrin	99.9999	99.9999	99.9999	99.9999
Carbon tetrachloride	99.9990	99.9951	99.9989	99.988
Propionaldehyde	99.963	99.998	99.750	99.687

99.9995, averaging 99.998 percent. CCl_4 DREs never went below the standard of 99.99 percent. DREs of other POHCs were generally higher than those for CCl_4. Analysis of semivolatile organic DREs was also conducted, and the average DRE was found to exceed 99.9999 percent.

Engineering-Science Study, 1984[9]--

Engineering-Science conducted a field test program at a packaged fire-tube boiler burning a mixture of toluene and chlorinated solvents. Two blends were fired, No. 1 containing 98 percent by weight of toluene, and No. 2 containing 97 percent by weight of toluene. The chlorinated solvents were carbon tetrachloride, trichloroethylene and chlorobenzene.

The boiler was a small capacity fire-tube boiler, with a high heat release capacity (92,000 Btu/hr ft^2) and high energy liberation rate (164,400 Btu/hr ft^3). The boiler was selected as a "worst-case situation for destroying hazardous wastes" in a boiler. The boiler operated at high combustion temperatures, short residence times, and an excess air range of 17 to 50 percent. Liquid waste injection was performed through a forced air venturi nozzle designed to fire gas or distillate oil. Six different operating load and excess air conditions were employed during the tests.

DREs, as shown in Table 12.9, for toluene, carbon tetrachloride, and trichloroethylene ranged from 99.9976 to 99.9999 Chlorobenzene DREs were lower, ranging from 99.948 through 99.978. Conditions were not adequate to achieve effective chlorobenzene destruction, but the boiler was able to effectively destroy the other three sample compounds. However, correlations between DRE and excess air and operating load were not apparent. The high combustion temperature achieved at the nozzle may be the key to the high DREs observed, despite the short residence times experienced.

GCA Study (Reference 7, 1984)--

A test program was conducted for the U.S. EPA/OSW to characterize the performance of six small commercial sized boilers (0.5 to 12.5 x 10^6 Btu/hr input) burning waste oil containing hazardous constituents. The waste oil burned throughout the test program was prepared from a supply of used oil purchased in bulk from a commercial vendor. The "basestock" oil (Higher Heating Value - 16, 350 Btu/lb) was spiked with several organic chemical compounds, including:

TABLE 12.9. RESULTS OF ENGINEERING-SCIENCE INDUSTRIAL BOILER TEST PROGRAM

Test no.	Boiler load/ excess air %	Toluene	DRE (%)		
			CCl_4	TCE	PCB
1	half/38	99.9997	99.9979	99.9999	99.952
3	half/31	99.9992	99.9990	99.9995	99.978
5	half/50	99.9991	99.9993	99.9976	99.972
2	full/38	99.9991	99.9989	99.9998	99.946
4	full/41	99.9994	99.9996	99.9999	99.948
6	full/17	99.9991	99.9992	99.9996	99.973
Average DREs		99.9993	99.9990	99.9994	99.961

- chloroform
- 1,1,1-trichloroethane
- trichloroethylene
- tetrachloroethylene (perchloroethylene)
- trichlorobenzene
- 1-chloronaphthalene
- 2,4,5,-trichlorophenol

These compounds were blended with the base oil at the time of the test. The concentration of POHCs spiked into the waste was varied widely both from one boiler site to another, and for separate tests conducted at the individual sites. Concentrations of each POHC ranged between 1,500 and 10,000 ppm. Stack gases were collected and sampled for organics and certain specific metal and HCl emissions. The destruction and removal efficiency was calculated for each POHC for each test run, as were metals and HCl emissions.

DRE results are presented in Table 12.10. As shown, DRE consistently exceeded 99 percent, but seldom were as high as 99.99 percent. DRE correlated fairly closely to concentration, as was noted in the Reference 5 study.

Emissions of particulate matter, HCl, and a variety of toxic heavy metals were measured in the gas stream. In keeping with data found in several studies of waste oil combustion, roughly 60 percent of the lead and 75 percent of the ash were emitted in the gas stream. Chlorine emissions, primarily as hydrogen chloride, were close to stochiometric, accounting for 86 percent of the chlorine in the feed.

12.2.2 Industrial Kilns and Other High Temperature Industrial Processes

The performance of various high temperature industrial unit processes firing hazardous wastes as a fuel has been subject to limited study.[12] Most of the analyses have focused upon the industrial rotary kilns, which appear to represent the most commercially viable hazardous waste management alternative. In general, the studies[8,11-13,14] have shown that such units are capable of effectively destroying POHCs.

DREs appear to be strongly correlated to the concentration of a POHC in a waste: the highest DREs for a constituent are associated with the largest concentration. In general, highly chlorinated waste constituents were cited as presenting the greatest difficulty in achieving high DREs.

TABLE 12.10. CALCULATED DESTRUCTION AND REMOVAL EFFICIENCIES (PERCENT)

	A	C	D	E	F	G	Average by compound
Boiler Data							
Rated Capacity (10^6 Btu/hr)	0.5	2.4	2.4	3.4	4.2	12.5	
Fuel Feed Rate (gal/hr)	3.19	24.05	13.14	14.6	23.6	23.1	
Volatile Compounds							
Chloroform	99.65	99.91	99.96	99.90	99.94	99.95	99.88
Trichloroethane	99.78	99.95	99.97	99.37	99.80	99.93	99.80
Trichloroethylene	99.45	99.92	99.89	99.85	99.92	99.87	99.82
Perchloroethylene	99.74	99.91	99.86	99.73	99.85	99.96	99.84
Semivolatile Compounds							
Trichlorobenzene	99.84	99.98	99.96	99.90	≥99.96	99.89	>99.92
1-chloronaphthalene	99.95	99.95	99.95	>99.94	99.98	99.92	>99.95
2,4,5-trichlorophenol	>99.97	>99.99	---	≥99.92	≥99.98	---	>99.97

Source: Reference 7.

Emissions of particulate matter and hydrogen chloride appeared to be reasonably well controlled by the systems, although extensive emissions data were seldom provided. Most of the systems tested did not employ an acid gas scrubbing system for HCl control. Emissions control is considered a primary limitation to using hazardous wastes as fuels, due to the expense involved in establishing and maintaining such systems. A probable contributor to the relatively low volume of emissions noted in the references is that the wastes burned in the tests did not have large chloride or ash contents. This represents the expected typical use-as-fuel application, as high chloride and ash contents tend to negatively impact the quality of the product of these processes.

Emissions of other pollutants of concern, such as heavy metals, were not discussed in great detail. As with highly chlorinated wastes, wastes containing higher concentrations of heavy metals probably would not be good candidates for use-as-fuel because of high particulate emission levels and potentially negative impacts upon product quality.

A brief summary of the major studies of using hazardous wastes as fuels in industrial processes, for which documentation is available, is presented below.

Engineering-Science Study (Reference 13)

Three separate asphalt plants were tested by Engineering-Science, to determine their effectiveness in destroying waste oils spiked with tetrachloroethylene (a.k.a., perchloroethylene) and chlorobenzene.

With the exception of metal analysis, composition data for the recycled oil fuels were not provided. Metals concentration in the waste fuel, with the exception of chromium and lead, were generally well below levels that would impact on levels in the aggregate produced by the plant.

DREs were measured at two of the plants. The measurement techniques employed during this test program were not adequate to provide a clear representation of DRE. DREs at Plant A were higher than those obtained at Plant B. At Plant A, an average DRE of 99.99 percent was achieved for perchloroethylene and chlorobenzene. At Plant B, the RCRA incinerator permit standard of 99.99 percent DRE was never achieved for perchloroethylene or chlorobenzene.

Florida Solite Company (Reference 8, 1984)

Florida Solite Company operates an aggregate kiln fired with fuel containing crushed coal and waste organic liquids. The liquid wastes consist primarily of solvents, alcohols, ethers, still bottoms, and chlorinated hydrocarbons. Average DREs reported for the five test runs were higher than the standard of 99.99 percent, for each POHC. Toluene appears to be the easiest to destroy and remove, while tetrachloroethylene ("perc") is the most difficult.

Liquid waste fuel was reported to comprise 54 percent by weight of the fuel mixture burned during this test. The waste fuels contained a variety of organic constituents, including four POHCs; methyl ethyl ketone, methyl isobutyl ketone, toluene and tetrachloroethylene. The waste fuels were relatively high in heat content (above the typical "limit" of 8,500 Btu/lb many companies employ to determine the need for auxiliary fuel) but also high in ash content (6 to 15 percent), and relatively low in chloride content.

San Juan Cement Company (Reference 14, 1984)

The San Juan Cement Company manufactures Portland cement in a kiln fired with No. 6 oil and waste liquids. Wastes tested in this program (see Reference 14) consisted of typical waste shipments to the plant. Six waste fuel batches were used during the test program. All but one had heat contents well in excess of 10,000 Btu/lb. Three POHCs were in the waste oils; methylene chloride, chloroform, and carbon tetrachloride (CCl_4). The overall chlorine contents of the wastes burned during an extensive test program were high, ranging from 6.5 to 35 percent.

The destruction and removal efficiencies measured during this program were generally below the RCRA incinerator permit standard of 99.99 percent. Methylene chloride appears to have been destroyed most effectively, while CCl_4 was not effectively destroyed in the San Juan system. DRE was found to be linked to POHC concentration.

The San Juan cement kiln inability to achieve high destruction or removal efficiency was partially attributed to the lack of an adequate injection mechanism for the waste fuel, which was introduced unatomized, and also to the high level of chlorine in the waste.

Rockwell Lime Company

Rockwell Lime Company operates a kiln, fired with petroleum, coke and natural gas. To determine the feasibility of replacing natural gas fuel with a hazardous waste fuel, tests were conducted using a waste fuel spiked with tetrachloroethylene and trichloroethylene. The test results indicate that the lime kiln process is capable of achieving high DREs (>99.99 percent), while emissions remain lower than specified in RCRA permit standards.[8]

Blast Furnace Test (Reference 11, 1985)

Liquid organic wastes are used at one blast furnace as a source of heat and carbon content to supplement or replace coke. The blast furnace has been retrofitted with a liquid injection system to feed waste materials to the combustion zone. Combustion zone temperatures exceed 3000°F.

Liquid wastes blended with No. 6 oil were fed at approximately 60 gallons/minute, with recirculation. The waste employed for this test contained 10 POHCs, including high levels of toluene, o-xylene, tetrachloroethylene, trichloroethylene and 1,1-dichloroethylene. The total chlorine content of the waste was found to be 835 ppm by weight.

High levels of destruction were achieved for most of the POHCs. Lower DREs were noted, however, for benzene and naphthalene, DRE correlated somewhat with concentration; with the exception of trichloroethane, high DREs were achieved for those compounds which were found in high concentration in the waste feed.

12.3 COST OF TREATMENT

The use of hazardous wastes as a fuel could provide significant economic benefits. The amount of virgin fuel consumed would be greatly reduced, resulting in potentially large savings in overall fuel costs. Waste use in boilers and industrial process equipment could also greatly reduce or eliminate capital costs for conservation of waste disposal alternatives, particularly if suitable process equipment is already in place at industrial facilities. If this equipment can be used, thereby avoiding the need for additional waste treatment facilities, large cost savings can be realized.

Estimation of the costs associated with hazardous waste fuel burning involves assessment of equipment capital costs, maintenance and labor costs, raw materials costs, disposal costs, liability costs, transportation costs, and energy costs. The costs may vary quite a bit from case to case, depending upon waste characteristics and system design. Some of the more important cost considerations are discussed below.

12.3.1 Capital Costs

The capital costs of the high temperature industrial process facilities suitable for combustion of hazardous wastes may be very high, depending upon the heat input capacity and the characteristics of wastes they may handle. In general, however, the costs of designing, purchasing, and implementing those systems is not in the multimillion dollar range found for hazardous waste incinerators. Even greater savings in capital expenditure can be realized if existing equipment can be retrofitted for hazardous waste combustion.

As stated by McCormick and Weitzman,[15] there are three primary components to the retrofit cost:

1. Addition of waste storage and feeding equipment;
2. Modification of combustion systems to handle additional physical stresses of burning hazardous wastes (e.g., corrosion resistant parts); and
3. Installation of air pollution control devices capable of handling additional particulate matter, HCl, and other pollutants as required by regulations.

The costs involved in storage and feeding, and combustion system modification can be high--storage tanks equipped specifically to handle hazardous waste liquids may cost in the $35,000 to $70,000 range for capacities ranging from 5,000 to 20,000 gallons, but the most significant retrofit cost element is the air pollution control system. HTIPs are generally not equipped with APC systems which have the capabilities required for control of hazardous waste combustion products. It is likely that some additional APC will be required, depending upon waste characteristics. In those cases where both the particulate loading and HCl loading require significant control, it may be desirable from a cost perspective to utilize APC systems which are capable of controlling both; e.g., a high energy scrubber.

Actual capital cost data are readily available from APC equipment vendors. Estimation of the engineering design, construction, and other costs may be done using standard cost estimation texts or through use of guidelines provided in Reference 15.

12.3.2 Fuel Cost Savings

The money saved as a result of substituting wastes for fuels is the most significant cost factor associated with this management alternative. Fuel savings may be estimated through an energy balance. As shown below, the amount of fuel saved is equivalent to the amount of fuel required to produce an equivalent amount of heat energy when burned at the level of efficiency the system is capable of attaining for that waste:

$$x_f = \frac{H_w \, E_w \, x_w}{H_f \, E_f}$$

where: x_f = quantity of fuel, lbs/hr

H_f = heat content of fuel, Btu/lb

E_f = HTIP combustion efficiency when fired with fuel

x_w = quantity of waste fuel, lbs/hr

H_w = heat content of waste fuel, BTU/lb

E_w = HTIP combustion efficiency when fired with waste fuel

The fuel cost savings is then calculated as follows:

$$C_f = x_f \, P_f - x_w P_w$$

where P = unit price of fuel or waste, $/lb

C_f = cost savings, $/hr

The correspondence between amount of fuel replaced and dollars saved may not be exactly linear, as the long term effects of burning hazardous wastes will tend to result in lower combustion efficiency and higher maintenance costs. Maintenance costs comprise a potentially significant portion of the overall operating costs of a waste fuel burning system. The two factors that contribute to higher maintenance requirements are the corrosivity of the waste and/or acid gas byproducts, and the degree to which plugging or fouling of the system; (e.g., by metallic or resinous waste constituents) will occur. Air pollution control systems often require the highest level of maintenance, and thus contribute most significantly to maintenance costs.

12.4 STATUS OF DEVELOPMENT

12.4.1 Availability/Application

Although the use of waste oil as a fuel in industrial, commercial, and even residential boilers has been a subject or interest for decades, the practice does not appear to have grown appreciably. Interest fostered by the high oil prices of past years has dropped as oil has become cheaper and more plentiful. Technological requirements necessary to achieve 99.99 DRE appear to be within the capability of most commercially available combustion equipment. However, each waste must be considered in view of its specific characteristics to determine if viscosity and chemical content, for example, are consistent with good combustion and acceptable emissions. The technology for predicting technical performance and emissions is well developed. However, the costs of new equipment or the retrofit of existing equipment must be contrasted with other available alternatives. These include offsite disposal in commercial incinerators or industrial process units.

While in most cases hazardous wastes will be burned as a fuel at the generator site, the disposal of hazardous wastes by combustion in a permitted commercial kiln or boiler site exists as an alternative to destruction in a hazardous waste incinerator. Only a handful of commercial HTIP facilities are currently in operation in the U.S., burning hazardous waste. Because these facilities derive an economic value from burning the wastes, the prices they charge for hazardous waste disposal are well below those of hazardous waste incinerators. The types of wastes which may be burned, however, is somewhat limited.

A company involved in this management alternative is the Systech Corporation, which operates cement kilns in several states that are capable of high level hazardous waste destruction. As noted earlier, Systech sets limits on the characteristics of wastes they can burn, primarily because of the effect waste burning will have on the quality of their cement. Charges for hazardous waste destruction will vary depending upon these characteristics. Presently they range from roughly 15 to 25 cents per gallon, based on 5,500 gallon tank lots. The actual prices depend on several factors, including the location of the facility.

12.4.2 Environmental Impact

The combustion of hazardous wastes as fuels or as constituents of fuels in high temperature industrial processes produces both air emissions and liquid and solid effluent streams. Generation of pollution by these processes must often be controlled, either through implementation of process equipment, such as air pollution control (APC) systems, or through the restriction of wastes that may be burned in a system. Environmental impacts associated with combustion or incineration often, therefore, constitute a primary determinant of the applicability of a specific system to a specific waste.

As indicated previously, many of the HTIPs selected as primary candidates for this application effectively control the emission of particulate matter; however, the control of other pollutants, most notably HCl vapor emissions, often presents significant problems. Environmental control is often prohibitively expensive for smaller facilities, requiring large capital expenditures for equipment, disposal and handling costs, labor and training.

EPAs regulations on burning hazardous wastes in HTIPs were changed as a result of the 1984 RCRA Amendments. Previously, any hazardous waste burned to recover energy value was exempted from regulation as a hazardous waste (and thus were not required to be handled or achieve emissions levels for incinerators established under EPA guidelines). In consideration of the potential risks to human health and the environment posed by the activities involved, the regulations were changed such that wastes must meet certain criteria to become exempted. Recent and proposed Federal regulatory developments include the following:

- Section 204 of the Hazardous and Solid Waste Amendments of 1984 (HWSA) amended RCRA Sections 3003, 3004, and 3010 to require notification and regulation of persons burning hazardous wastes or hazardous waste derived fuels;
- By February 8, 1986, notification must have been furnished to EPA or to Directors of authorized State programs by owners and operators of any facility burning any hazardous waste or used oil for purposes of energy recovery;
- By November 8, 1986, the Administrator must publish such standards as may be necessary to protect human health and the environment by regulating owners and operators of facilities burning any fuel containing any hazardous waste;
- "Hazardous waste" for this purpose is defined in HWSA as including any commercial chemical product listed in 40 CFR 261.33 which is burned as a fuel in lieu of its originally intended use; and
- EPA may exempt from hazardous waste management standards facilities which burn "de minimis" quantities of hazardous waste for energy recovery, if the combustion takes place at the generation site, and environmentally sound practices are otherwise employed.

The regulation of hazardous waste combustion in HTIPs at the State level is focussed upon the applicable combustion units and the generation of air emissions. Generally, the facilities in which hazardous waste fuels may be burned are specified in the regulations, for example, in Massachusetts the burning of hazardous waste fuel is prohibited except in:

a. An industrial and utility boiler or an industrial furnace permitted or licensed by the state for that burning;

b. A hazardous waste incinerator licensed pursuant to 310 CMR 7.00 and 30.000; or

c. A cement kiln located within the boundaries of a municipality with a population less than 50,000 (based on the most recent census statistics) if such cement kiln is in full compliance with all requirements of 310 CMR 30.000 and 7.08 applicable to hazardous waste incinerators.[16]

No special conditions apply to the liquid or solid effluent streams from those processes. Thus, if scrubber sludges or bottom ash from a system burning wastes as fuel itself contains hazardous constituents, they must be disposed of in the same manner as similar materials generated differently; e.g., stabilized and in a secure landfill.

Air emissions standards applicable to combustion of hazardous wastes in HTIPs vary from State to State. No State currently has implemented a comprehensive air toxics emission program, although several States appear to be developing such standards. Regulation of air toxics would have significant impact upon hazardous waste fuel burning particularly since HTIPs may not achieve destruction or control levels comparable to those of incinerators.

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SECTION 13.0

LAND DISPOSAL OF RESIDUALS

Land disposal of solvent wastes is not likely to be achievable without risk to human health and the environment unless treatment is undertaken prior to disposal. Treatment such as pyrolysis and incineration lead to destruction of the waste constituents of concern and the residuals (e.g., ash and scrubber wastes) have proven to be nonhazardous (see Section 10). Other treatments such as carbon or resin adsorption effectively reduce concentration levels in aqueous media to below standards felt to be nonhazardous. However, the constituents in this case are not destroyed but are merely collected and concentrated on the sorbent surface. The sorbent then must be treated, possibly incinerated, to eliminate the risks associated with the presence of these hazardous constituents. In the absence of the possibility of land disposal of waste in a location that will be demonstrably supportive of human health and the environment (e.g., deepwell injection), another option is to treat the waste to immobilize the waste constituents for as long as they remain hazardous. This method of treatment, based on fixation or encapsulation processes, is a possibility for some solvent wastes; however, it is more likely a treatment that will be undertaken to ensure that residuals from other treatment processes can be safely disposed. Certain of these residuals could be found hazardous for reasons other than solvent content; e.g., their heavy metal content may lead to positive tests for EP toxicity. In such cases, encapsulation may be needed to eliminate this characteristic. As will be noted, fixation and encapsulation processes have not been demonstrated for solvent wastes, and it is not likely that high levels of organics (>20 percent) can be effectively treated by these techniques.

The following discussions will summarize available information concerning immobilization techniques, namely chemical fixation or encapsulation. Chemical fixation involves the chemical interaction of the waste with a binder; encapsulation is a process in which the waste is physically entrapped within a stable, solid matrix. Despite the interest shown in immobilization techniques and some generalizations made concerning their applicability to solvent wastes, there are little, if any, data provided in the literature. Most techniques described must be considered physical processes and few techniques can be considered to represent chemical fixation. Even if fixation could be demonstrated, little is known concerning the long term stability of the matrix and the possible breakdown products over time. In situ vitrification, a process described in Section 11, would appear to provide both destruction of hazardous constituents with encapsulation in a matrix of long term durability. It and the other processes described below, will require further study to demonstrate their effectiveness for solvent wastes. However, much will depend upon the regulatory criteria now being established by EPA for fixation/encapsulation processes.

13.1 SOLIDIFICATION/CHEMICAL FIXATION

Solidification can be used to chemically fix or structurally isolate solvent and ignitable wastes to a solid, crystalline, or polymeric matrix. The resultant monolithic solid mass can then be safely handled, transported, and disposed of using established methods of landfilling or burial. Solidification technologies are usually categorized on the basis of the principal binding media, and include such additives as: cement-based compounds, lime-based pozzolanic materials, thermoplasts, and organic polymers (thermosets). The resulting stable matrix produces a material that contains the waste in a nonleachable form, is nondegradable, cost effective, and does not render the land it is disposed in unusable for other purposes. A brief summary of the compatibility and cost data for selected waste solidification/stabilization systems is presented in Tables 13.1 and 13.2.

Cement Based Systems

These systems utilize type I Portland cement, water, proprietary additives, possibly fly ash, and waste sludges to form a monolithic, rock-like mass. In an EPA publication,[2] several vendors of cement based systems

TABLE 13.1. COMPATIBILITY OF SELECTED WASTE CATEGORIES WITH DIFFERENT WASTE SOLIDIFICATION/STABILIZATION TECHNIQUES

Waste component	Treatment Type						
	Cement based	Lime based	Thermoplastic solidification	Organic polymer (UF)*	Surface encapsulation	Self-cementing techniques	Glassification and synthetic mineral formation
Organics:							
1. Organic solvents and oils	May impede setting, may escape as vapor	Many impede setting, may escape as vapor	Organics may vaporize on heating	May retard set of polymers	Must first be absorbed on solid matrix	Fire danger on heating	Wastes decompose at high temperatures
2. Solid organics (e.g., plastics, resins, tars)	Good--often increases durability	Good--often increases durability	Possible use as binding agent	May retard set of polymers	Compatible--many encapsulation materials are plastic	Fire danger on heating	Wastes decompose at high temperatures
Inorganics:							
1. Acid wastes	Cement will neutralize acids	Compatible	Can be neutralized before incorporation	Compatible	Can be neutralized before incorporation	May be neutralized to form sulfate salts	Can be neutralized and incorporated
2. Oxidizers	Compatible	Compatible	May cause matrix break down, fire	May cause matrix break down	May cause deterioration of encapsulating materials	Compatible if sulfates are present	High temperatures may cause undeable reactions
3. Sulfates	May retard setting and cause spalling unless special cement is used	Compatible	May dehydrate and rehydrate causing splitting	Compatible	Compatible	Compatible	Compatible in many cases
4. Halides	Easily leached from cement, may retard setting	May retard set, most are easily leached	May dehydrate	Compatible	Compatible	Compatible if sulfates are also present	Compatible in many cases
5. Heavy metals	Compatible	Compatible	Compatible	Acid pH solubilizes metal hydroxides	Compatible	Compatible if sulfates are present	Compatible in many cases
6. Radioactive materials	Compatible	Compatible	Compatible	Compatible	Compatible	Compatible if sulfates are present	Compatible

* Urea-Formaldehyde resin.

Source: Reference 1.

TABLE 13.2. PRESENT AND PROJECTED ECONOMIC CONSIDERATIONS FOR WASTE SOLIDIFICATION/ STABILIZATION SYSTEMS

Type of treatment system	Major materials required	Unit cost of material	Amount of material required to treat 100 lbs of raw waste	Cost of material required to treat 100 lbs of raw waste	Trends in price	Equipment costs	Energy use
Cement-based	Portland Cement	$0.03/lb	100 lb	$ 3.00	Stable	Low	Low
Pozzolanic	Lime Flyash	$0.03/lb	100 lb	$ 3.00	Stable	Low	Low
Thermoplastic (bitumen-based)	Bitumen Drums	$0.05/lb $27/drum	100 lb 0.8 drum	$18.60	Keyed to oil prices	Very high	High
Organic polymer (polyester system)	Polyester Catalyst Drums	$0.45/lb $1.11/lb $17/drum	43 lb of polyester-catalyst mix	$27.70	Keyed to oil prices	Very high	High
Surface encapsulation (polyethylene)	Polyethylene	Varies	Varies	$ 4.50*	Keyed to oil prices	Very high	High
Self-cementing	Gypsum (from waste)	**	10 lb	**	Stable	Moderate	Moderate
Glassification/mineral synthesis	Feldspar	$0.03/lb	Varies	—	Stable	High	Very high

* Based on the full cost of $91/ton.

** Negligible but energy cost for calcining are appreciable.

Source: Reference 1.

reported problems with organic wastes containing oils, solvents, and greases not miscible with an aqueous phase. For although the unreactive organic wastes become encased in the solids matrix, their presence can retard setting, cause swelling, and reduce final strength.[3] These systems are most commonly used to treat inorganic wastes such as incinerator generated wastes and heavy metal sludges.

Lime Based (Pozzolanic) Techniques

Pozzolanic concrete is the reaction product of fine-grained aluminous siliceous (pozzolanic) material, calcium (lime), and water. The pozzolanic materials are wastes themselves and typically consist of fly ash, ground blast furnace slag, and cement kiln dust. The cementicious product is a bulky and heavy solid waste used primarily in inorganic waste treatment such as the solidification of flue gas desulfurization sludge. However, biological and paint sludges have been treated, although high concentrations (greater than 20 percent) of organics tend to prevent the formation of a high strength product.[4]

Thermoplastic Material

In a thermoplastic stabilization process, the waste is dried, heated (260-450°F), and dispersed through a heated plastic matrix. Principal binding media include asphalt, bitumen, polypropylene, polyethylene, or sulfur. The resultant matrix is resistant to leaching and biodegradation, and the rates of loss to aqueous contacting fluids are significantly lower than those of cement or lime based systems. However this process is not suited to wastes that act as solvents for the thermoplastic material. Also there is a risk of fire or secondary air pollution with wastes that thermally decompose at high temperature.[1]

Organic Polymers (Thermosets)

Thermosets are polymeric materials that crosslink to form an insoluble mass as a result of chemical reaction between reagents, with catalysts sometimes used to initiate reaction. Waste constituents could conceivably enter into the reaction, but most likely will be merely physically entrapped within the crosslinked matrix. The crosslinked polymer or thermoset will not soften when heated after undergoing the initial set. Principal binding agents or reactants for stabilization include ureas, phenolics, epoxides, and polyesters. Although the thermosetting polymer process has been used most frequently in the radioactive waste management industry, there are formulations that may be applicable to certain organic contaminants. It is important to note that the concept of thermoset stabilization, like thermoplastic stabilization, does not require that chemical reaction take place during the solidification process. The waste materials are physically trapped in an organic resin matrix that, like thermoplastics, may biodegrade and release much of the waste as a leachate.[5] It is also an organic material that will thermally decompose if exposed to a fire.

New Technology

An EPA sponsored study recently indicated that most solidification processes in current use (silicates, lime, and cement), including those described above, stabilize contaminants through microencapsulation rather than chemical fixation.[6] Microencapsulation is a process that entraps micro and macroscopic particles individually as the fixative solidifies. An inorganic polymer that is a candidate for true chemical fixation is the HWT product series marketed by International Waste Technologies. The HWT series is a set of inorganic, irreversible colloidal polymers which improve on a successful Japanese approach which has been used in Japan for over 10 years.

In the HWT fixation process, there is a two-step reaction in which the toxic elements and compounds are complexed first in a rapid reaction and then permanently complexed in the building of macromolecules which continue to generate over a long period of time. Step one of the detoxification reaction is the blending of contaminants and HWT chemicals to achieve a homogeneous state so that all the toxic compounds are exposed. This blending generates irreversible colloidal structures and ion exchanges with toxic metals and organics. Step two is the generation of an irreversible, three-dimensional, macromolecule which provides the crosslinking framework. The vendor claims that both inorganic and organic wastes are treatable in either concentrated or dilute form, although pretreatment may be necessary. Table 13.3 shows the effect of the inorganic polymer on samples of PCB and PCP. The levels of toxic compounds before and after treatment were determined by EPA approved laboratory testing. A company spokesman indicated that data on the effectiveness of HWT on concentrated trichloroethylene still bottoms will be available in the near future.[7]

TABLE 13.3. SUMMARY OF TEST RESULTS ON TOXIC ORGANICS

Toxic organic (µg/L)	HWT - 20 weight percent	Concentration (µg/L)	
		Untreated	Treated
PCB	15	1,140	0.006
	15	1,800	0.069
	15	9,200	0.337
PCP	15	11,000	450

Source: International Waste Technology.

International Waste Technology has estimated average treatment levels by HWT compounds run between 8-15 percent by weight of waste with HWT compounds costing between 12-25¢/lb. The company estimates that heavy metal electric arc furnace dust could be treated for $19/ton while chemical still bottoms (halogenated hydrocarbons, benzene compounds, phenols in pure state) would cost $90-100/ton in materials costs for low volumes of waste. The bases for these cost estimates are not entirely clear. As a fixant for low molecular weight organics, it would appear that HWT amounts far greater than 8 to 15 percent by weight of waste would be required. At an assumeable level of 50:50 HWT/waste, costs would range from $120-250/ton for HWT material with additional costs required for transportation, processing, and disposal.

13.2 MACROENCAPSULATION

Encapsulation is often used to describe any stabilization process in which the waste particles are enclosed in a coating or jacket of inert material. A number of systems are currently available utilizing polybutadiene, inorganic polymers (potassium silicates), portland concrete, polyethylene, and other resins as macroencapsulation agents for wastes that have or have not been subjected to prior stabilization processes. Several different encapsulation schemes have been described in Reference 6. The resulting products are generally strong encapsulated solids, quite resistant to chemical and mechanical stress, and to reaction with water. Wastes (nonsolvent) successfully treated by these methods and their costs are summarized in Tables 13.4 and 13.5. The technologies could be considered for stabilizing organic wastes but are dependent on the compatibility of the organic waste and the encapsulating material. Additional research is needed concerning the interaction of organic wastes and stabilization materials and the durability of the matrix, if the safe disposal of wastes and treatment residuals is to be realized through these processes. EPA is now in the process of developing criteria which stabilized/solidified wastes must meet in order to make them acceptable for land disposal.(8)

TABLE 13.4. ENCAPSULATED WASTE EVALUATED AT THE U.S. ARMY WATERWAYS EXPERIMENT STATION

Code No.	Source of Waste	Major Contaminants
100	SO_x scrubber sludge, lime process, eastern coal	Ca, $SO_4^=/SO_3^=$
200	Electroplating sludge	Cu, Cr, Zn
300	Nickel - cadmium battery production sludge	Ni, Cd
400	SO_x scrubber sludge, limestone process eastern coal	Cu, $SO_4^=/SO_3^=$
500	SO_x scrubber sludge, double alkali process eastern coal	Na, Ca, $SO_4^=/SO_3^=$
600	SO_x scrubber sludge, limestone process, western coal	Ca, $SO_4^=/SO_3^=$
700	Pigment production sludge	Cr, Fe, CN
800	Chlorine production brine sludge	Na, Cl^-, Hg
900	Calcium fluoride sludge	Ca, F^-
1000	SO_x scrubber sludge, double alkali process, western coal	Cu, Na, $SO_4^=/SO_3^=$

TABLE 13.5. ESTIMATED COSTS OF ENCAPSULATION

Process Option	Estimated Cost
Resin Fusion:	
Unconfined waste	$110/dry ton
55-Gallon drums	$0.45/gal
Resin spray-on	Not determined
Plastic Welding	$253/ton = $63.40/drum (80,000 55-gal drums/year)

Source: Reference 6.

REFERENCES

1. Guide to the Disposal of Chemically Stabilized and Solidified Waste, EPA SW-872, Sept. 1980.

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5. Thompson, D.W. and Malone P.G., Jones, L.W., Survey of available stabilization technology in Toxic and Hazardous Waste Disposal, Vol. 1, Pojasek, R.B., Ed. Ann Arbor Science, Ann Arbor Michigan. 1979.

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7. Newton, Jeff, International Waste Technology, Personal communication, 1986.

8. C. Wiles, Hazardous Waste Engineering Research Laboratory, U.S. EPA, private communication; and Critical Characteristics and Properties of Hazardous Waste Solidification/Stabilization, HWERL, U.S. EPA, Contract No. 68-03-3186 (in publication).

SECTION 14.0

CONSIDERATIONS FOR SYSTEM SELECTION

Waste management options consist of three basic alternatives: source reduction, recycling/reuse, use of a treatment/disposal processing system or some combination of these waste handling practices (see Figure 14.1). Recovery, treatment, and disposal may be performed onsite in new or existing processes or through contract with a licensed offsite firm which is responsible for the final disposition of the waste. Selection of the optimal waste management alternative will ultimately be a function of regulatory compliance and economics, with additional consideration given to factors such as safety, public and employee acceptance, liability, and uncertainties in meeting cost and treatment objectives.

Many of the technologies discussed in previous sections can be utilized to achieve high levels of solvent removal or destruction; however, practicality will limit application to waste streams possessing specific characteristics. Since many processes yield large economies of scale, waste volume will be a primary determinant in system selection. The physical and chemical nature of the waste stream and pertinent properties of its constituents, including many of those properties identified in Appendix A, will also determine the applicability of waste treatment processes. Treatment will often involve the use of more than one technology in a system designed to progressively recover or destroy hazardous constituents in the most economical manner. Incremental costs of solvent removal will increase rapidly as low concentrations are attained.[1]

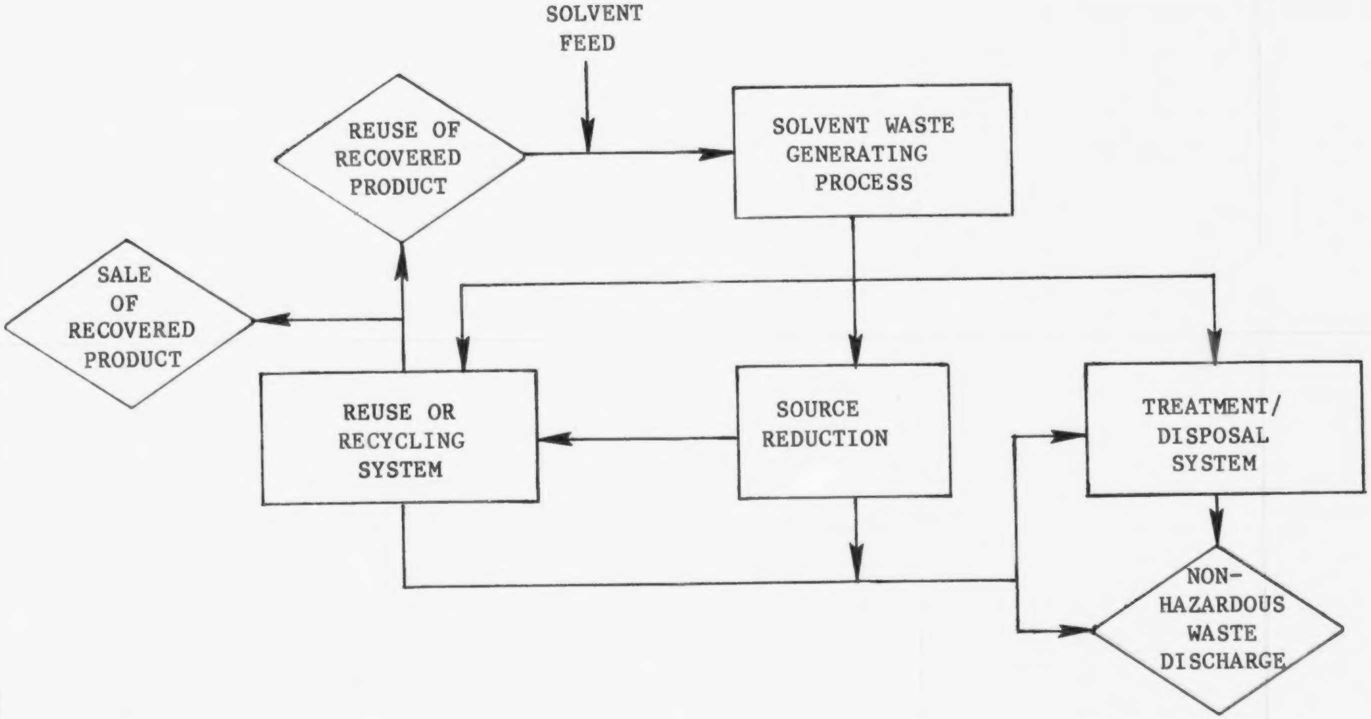
SOLVENT FEED
REUSE OF RECOVERED PRODUCT
SOLVENT WASTE GENERATING PROCESS
SALE OF RECOVERED PRODUCT
REUSE OR RECYCLING SYSTEM
SOURCE REDUCTION
TREATMENT/ DISPOSAL SYSTEM
NON-HAZARDOUS WASTE DISCHARGE

Figure 14.1. Solvent Waste Management Options

14.1 GENERAL APPROACH

All generators of hazardous solvent wastes will be required to undertake certain steps to characterize regulated waste streams and to identify potential treatment options. Treatment process selection should involve the following fundamental steps:

1. Characterize the source, flow, and physical/chemical properties of the waste.
2. Evaluate the potential for source reduction.
3. Evaluate the potential for reuse or sale of recycled solvent and other valuable waste stream constituents.
4. Identify potential treatment and disposal options based on technical feasibiltiy of meeting the required extent of solvent removal or destruction. Give consideration to waste stream residuals and fugitive emissions to air.
5. Determine the availability of potential options. This includes the use of offsite services, access to markets for recovered products, and availability of commercial equipment and existing onsite systems.
6. Estimate total system cost for various options, including costs of residual treatment and/or disposal and value of recovered solvent product. Cost will be a function of items 1 through 5.
7. Screen candidate management options based on preliminary cost estimates.
8. Use mathmatical process modeling techniques and lab/pilot scale testing as needed to generate detailed treatment system design characteristics and processing capabilities. The latter will define product and residual properties and identify need for additional treatment.
9. Perform process trials of recovered product in its anticipated end use applications or determine marketability based on projected stream characteristics.
10. Calculate detailed cost analysis based on modeling and performance results.
11. Final system selection based on relative cost and other considerations; e.g., safety, acceptance, liability, and risks associated with data uncertanties.

Key system selection steps are discussed in more detail below.

14.2 ASSESSMENT OF ALTERNATIVES

Waste Characterization

The first step in identifying appropriate waste management alternatives to land disposal involves characterizing the origin, flow, and quality of generated wastes. An understanding of the processing or operational practices which result in generation of the waste forms the basis for evaluating waste minimization options. Waste flow characteristics include quantity and rate. Waste quantity has a direct impact on unit treatment costs due to economies of scale in treatment costs and marketability of recovered products. Flow rate can be continuous, periodic, or incidental (e.g., spills) and can be relatively constant or variable. This will have a direct impact on storage requirements and treatment process design; e.g., continuous or batch flow.

Waste physical and chemical characteristics are generally the primary determinant of waste management process selection for significant volume wastes. Of particular concern is whether the waste is pumpable, inorganic or organic, and whether it contains recoverable materials, interfering compounds or constituents which may foul heat or mass transfer surfaces. Waste properties such as corrosivity, reactivity, ignitability, heating value, viscosity, concentrations of specific chemical constituents, biological and chemical oxygen demand, and solids, oil, grease, metals and ash content need to be determined to evaluate applicability of certain treatment processes. Individual constituent properties such as solubility, vapor pressure, partition coefficients, thermal stability, reactivity with various biological and chemical (e.g., oxidants and reductants) reagents, and adsorption coefficients are similarly required to assess treatability. Finally, variability in waste stream characteristics will necessitate overly conservative treatment process design and additional process controls. This will adversely affect processing economics and marketability of recovered products.

Source Reduction Potential

As discussed in Section 5.0, source reduction potential is highly site specific, reflecting the variablity of industrial waste generating processes and product requirements. Source reduction alternatives which should be investigated include raw material substitution, product reformulation, process redesign and waste segregation. The latter may result in additional handling and storage requirements, while differential processing cost and impact on product quality may be more important considerations for the other alternatives. Source reduction should be considered a highly desireable waste management alternative. In the wake of increasing waste disposal and liability costs, it has repeatedly proven to be cost effective while at the same time providing for minimal adverse health and environmental impact.

Recycling Potential

As part of the waste characterization step, the presence of potentially valuable waste constituents should be determined. Economic benefits from recovery and isolation of these materials may result if they can be reused in onsite applications or marketed as saleable products. In the former case, economic benefits result from decreased consumption of virgin raw materials. This must be balanced against possible adverse effects on process equipment or product quality resulting from buildup or presence of undesirable contaminants. Market potential is limited by the lower value of available quantity or demand. Market potential will be enhanced with improved product purity, availability, quantity, and consistency.

Identifying Potential Treatment and Disposal Options

Following an assessment of the potential for source reduction and recycling, the generator should evaluate treatment systems which are technically capable of meeting the necessary degree of solvent removal or destruction. Guideline considerations for the investigation of treatment technologies are summarized in Table 14.1. The treatment objectives for a waste stream at a given stage of treatment will define the universe of

TABLE 14.1. GUIDELINE CONSIDERATIONS FOR THE INVESTIGATION OF WASTE TREATMENT TECHNOLOGIES

A. Objectives of Treatment:

- Primary function (pretreatment, treatment, residuals treatment)
- Primary mechanisms (destruction, removal, conversion, separation)
- Recover waste for reuse (fuel, process solvent)
- Recovery of specific chemicals, group of chemicals
- Polishing for effluent discharge
- Immobilization or encapsulation to reduce migration
- Overall volume reduction of waste
- Selective concentration of hazardous constituents
- Detoxification of hazardous constituents

B. Waste Applicability and Restrictive Waste Characteristics:

- Acceptable concentration range of primary & restrictive waste constituents
- Acceptable range in flow parameters
- Chemical and physical interferences

C. Process Operation and Design:

- Batch versus continuous process design
- Fixed versus mobile process design
- Equipment design and process control complexity
- Variability in system designs and applicability
- Spatial requirements or restrictions
- Estimated operation time (equipment down-time)
- Feed mechanisms (wastes and reagents; solids, liquids, sludges, slurries)
- Specific operating temperature and pressure
- Sensitivity to fluctuations in feed characteristics
- Residuals removal mechanisms
- Reagent requirements
- Ancillary equipment requirements (tanks, pumps, piping, heat transfer equipment)
- Utility requirements (electricity, fuel and cooling, process and make-up water)

D. Reactions and Theoretical Considerations:

- Waste/reagent reaction (destruction, conversion, oxidation, reduction)
- Competition or suppressive reactions
- Enhancing conditions (specify chemicals)
- Fluid mechanics limitations (mass, heat transfer)
- Reaction kinetics (temperature and pressure effects)
- Reactions thermodynamics (endothermic/exothermic/catalytic)

(continued)

TABLE 14.1 (continued)

E. Process Efficiency:

- Anticipated overall process efficiency
- Sensitivity of process efficiency to:
    - feed concentration fluctuations
    - reagent concentration fluctuations
    - process temperature fluctuations
    - process pressure fluctuations
    - toxic constituents (biosystems)
    - physical form of the waste
    - other waste characteristics
- Acceptable range of fluctuations

F. Emissions and Residuals Management:

- Extent of fugitive and process emissions and potential sources (processing equipment, storage, handling)
- Ability (and frequency) of equipment to be "enclosed"
- Availability of emissions data/risk calculations
- Products of incomplete reaction
- Relationship of process efficiency to emission data
- Air pollution control device requirements
- Process residuals (cooling and scrubber water, bottom ash, fly ash, fugitive/residual reagents, recovered products, filter cakes, sludges)
- Residual constituent concentrations and leachability
- Delisting potential

G. Safety Considerations:

- Safety of storing and handling wastes, reagents, products and residuals
- Special materials of construction for storage and process equipment
- Frequency and need for use of personnel protection equipment
- Requirements for extensive operator training
- Hazardous emissions of wastes or reagents
- Minimization of operator contact with wastes or reagents
- Frequency of maintenance of equipment containing hazardous materials
- High operating temperatures or pressures
- Difficult to control temperatures or pressures
- Resistance to flows or residuals buildup
- Dangerously reactive wastes/reagents
- Dangerously volatile wastes/reagents

candidate technologies. Restrictive waste characteristics (e.g., concentration range, flow, interfering compounds) and technological limitations of candidate treatment processes will reduce this to a list of potential applications for a specific waste. Consideration must be given to pretreatment options for eliminating restrictive waste characteristics, process emissions, residuals and their required treatment, and opportunities for by-product recovery. System design will be based on the most difficult compound to remove or destroy.

A number of approaches to selecting potential treatment technologies for solvent waste streams have been proposed[1-11]. Many of these references also provide cost information to assist the user in making a final determination of the cost effectiveness of a process. One scheme that specifically addresses the management of solvent bearing wastes is that proposed by Blaney in Reference 3. Management alternatives including recycle/reuse, destructive treatments such as those resulting from thermal oxidations, and treatments for the removal of solvents prior to land disposal are reviewed. The reference discusses the applicability of these waste management alternatives to solvent waste streams having various physical chaaracteristics. Several waste treatment techniques are described including incineration, agitated thin film evaporation, fractional distillation, steam stripping, wet oxidation, carbon adsorption, and activated sludge biological treatment.

Blaney discusses approaches to treating three broad categories of solvent bearing waste: 1) aqueous and mixed aqueous/organic liquids, 2) organic liquids, and 3) sludges. As defined here, aqueous streams have water contents of 95 percent of higher, while organic streams are described as containing 50 percent or more organic liquids. Mixed aqueous/organic streams fall in between. Sludges are streams with solids content greater than 2 percent. Decision charts for aqueous and mixed aqueous/organic liquids and for organic liquids waste stream treatment are provided in Figures 14.2 and 14.3. Discussion of these charts in Reference 3 identifies some possible treatment options and stresses the importance of the possible need for treatment of residuals.

The treatment processes potentially applicable to the three broad categories of waste are shown in Table 14.2. The identification of potentially applicable treatment processes should be considered as tentative

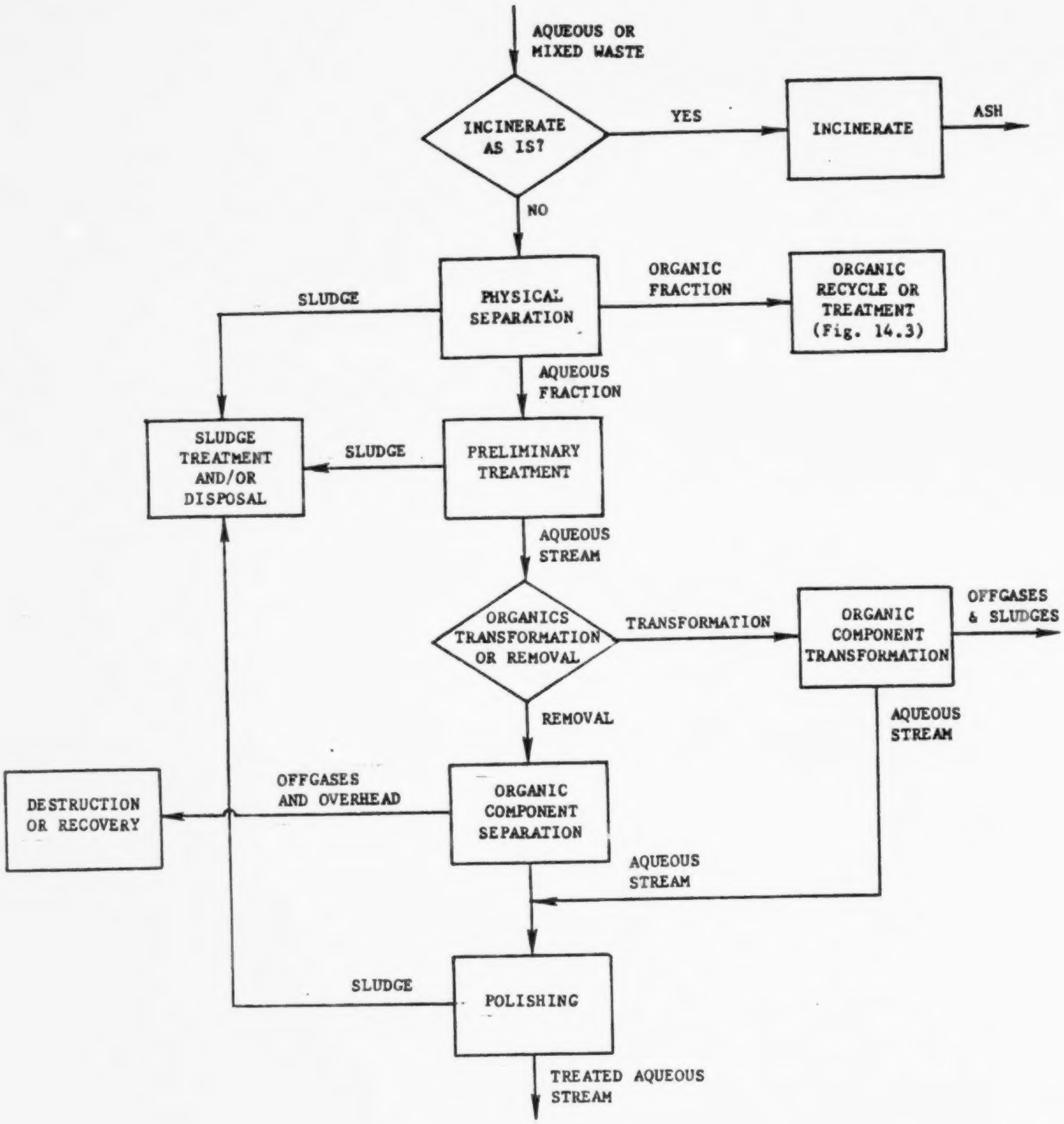

Figure 14.2. Simplified decision chart for aqueous and mixed aqueous/organic solvent waste stream treatment.
Source: Reference No. 3.

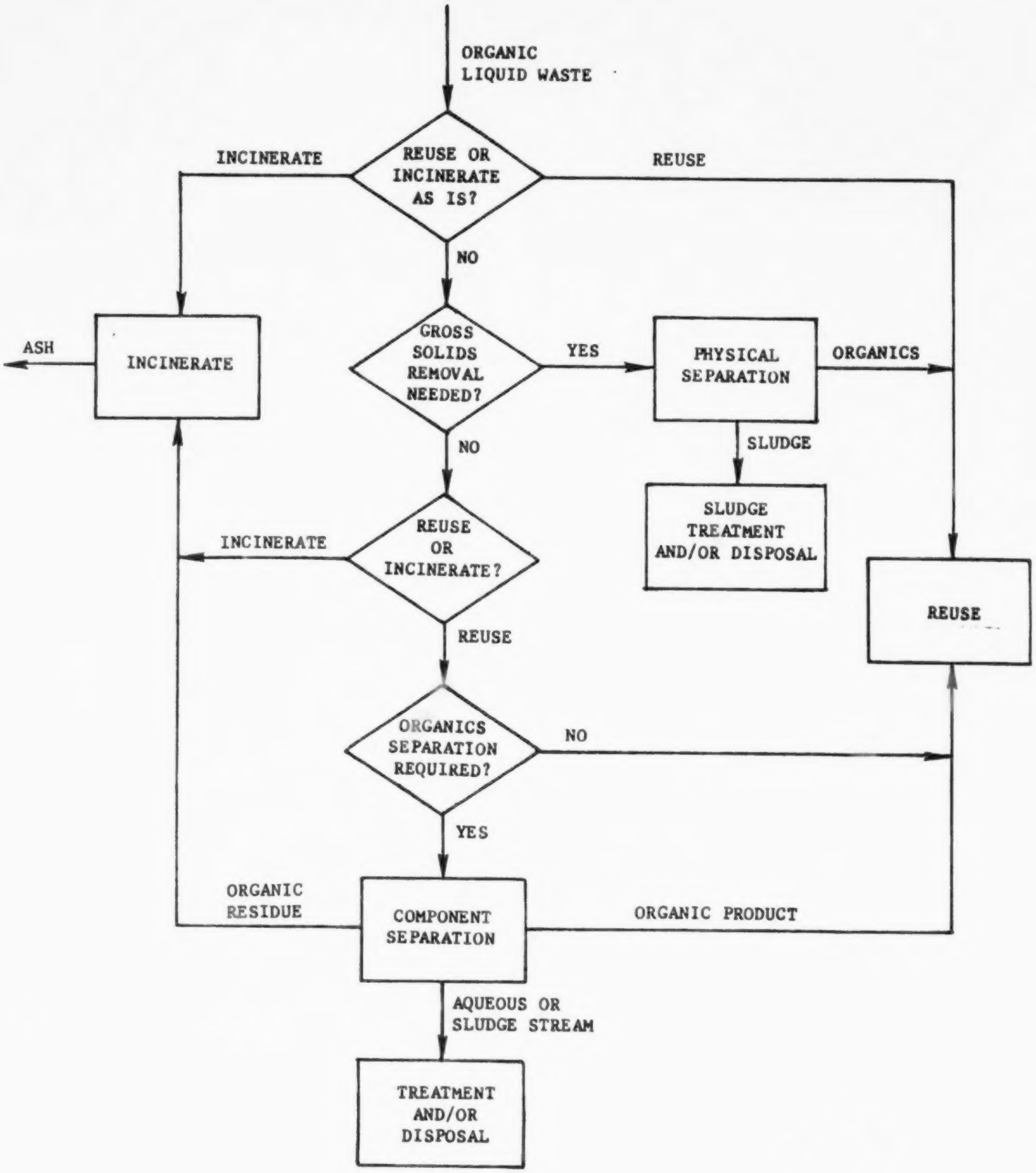

Figure 14.3. Simplified decision chart for organic liquid solvent waste stream treatment.
Source: Reference No. 3.

TABLE 14.2. TREATMENT PROCESSES POTENTIALLY APPLICABLE TO SOLVENT WASTES

Process	Aqueous and mixed aqueous/ organic wastes	Organic wastes	Sludges
Preliminary Treatment			
pH adjustment	Y	NA	NA
Dissolved solid precipitation	Y	NA	NA
Phase Separation			
Solids removal	Y	Y	NA
Drying	NA	Y	Y
Organic fraction	Y	Y	Y
Organic Component Separation			
Air or stream stripping	Y	Y	Y
Carbon adsorption	Y	NA	NA
Fractional distillation	Y	Y	Y
Resin adsorption	Y	Y	NA
Solvent extraction	Y	Y	Y
Organic Compound Destruction			
Incineration	Y	Y	Y
Biological degradation	Y	NA	NA
Chemical oxidation	Y	NA	NA
Wet oxidation	Y	NA	Y
Supercritical water	Y	NA	NA
Stabilization/Solidification	NA	NA	Y

Y = Yes

NA = Generally not applicable.

Source: Adapted from Reference 3

since the treatments used will depend upon specific waste stream characteristics not fully defined by the three general waste categories and the purpose of the treament. In addition, other innovative and emerging technologies described in previous sections of this document could also be considered as applicable processes for some of these waste categories.

Concentration of organic solvent within the waste categories is a principal determinant in assessing the applicability of a treatment process. Concentration ranges for which treatment processes are generally applicable are shown in Figure 14.4. Generally, techniques used for wastes with organic concentrations over 10 percent are applicable to lower concentrations as well, but other processes are generally more economical. Other waste characteristics which affect process selection are waste viscosity and solids content and contaminant type, volatility, and solubility. Viscosity is important in that it indicates whether the waste stream is sufficiently fluid to undergo treatment. If not, high temperature to improve flow properties or treatment such as incineration in a kiln may be required. The presence of excess solids can cause plugging of certain equipment such as packed towers and necessitate solids removal prior to treatment. Dissolved solids may also require removal if they precipitate or otherwise interfere with process performance. Solubility and volatility are indicators of the ease of removal of a volatile compound by processes such as distillation or stripping. Finally, the type of contaminant will play a role in process selection. Certain types of compounds may be susceptible to reaction and degradation, and may, as in the case of halogens, produce corrosive byproducts and be inherently low in Btu value.

A list of hazardous solvents and other low molecular weight organic compounds and their amenability to biological and chemical treatment and incineration is provided in Table 14.3. The information provided in this table is necessarily general since the characteristics of the solvent matrix will greatly influence performance. Reference 10 presents a similar table assessing the applicability of waste treatment processes to various model waste streams and their constituents. A letter grade is provided for every combination of treatment technique and waste stream constituent. Order of magnitude (±50 percent) costs are presented for example waste streams and technologies.

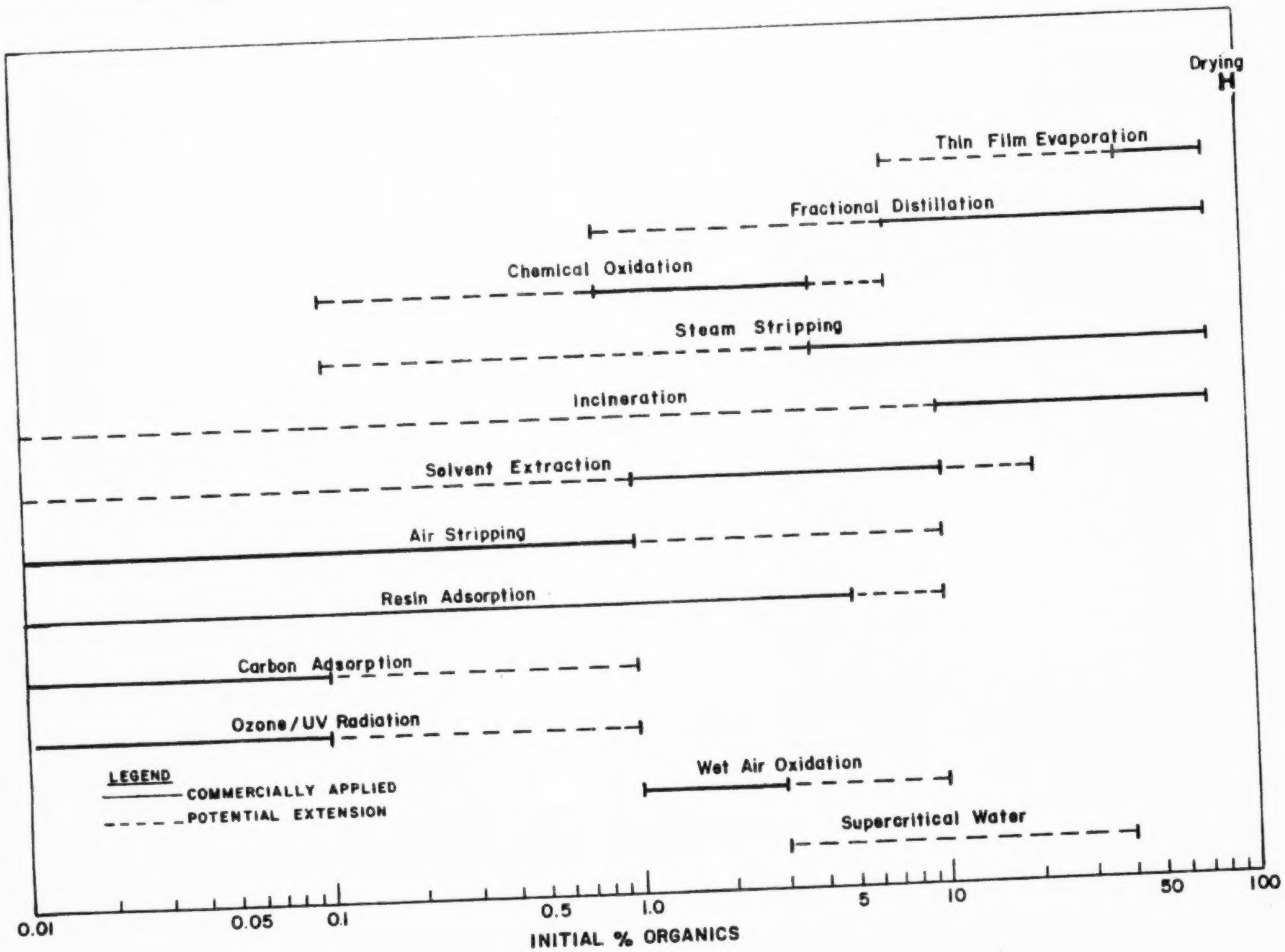

Figure 14.4. Approximate ranges of applicability of treatment techniques as a function of organic concentration in liquid waste streams.

Source: References 1 and 11.

TABLE 14.3. LIST OF HAZARDOUS CONSTITUENTS AND TREATMENT OPTIONS

Constituent	Amenable to conventional biological treatment	Amenable to aqueous chemical treatment	Amenable to incineration
Solvents of Concern			
1,1,1-Trichloroethane	NA	NA	Y
1,1,2-Trichloro-1,2,2-Trifluroroethane	NA	NA	Y
1,2-Dichlorobenzene	Y	N	Y
1-Butanol	Y	N	Y
Acetone	Y	Y	Y
Carbon Disulfide	N	N	Y
Carbon Tetrachloride	N	N	Y
Chlorobenzene	Y	N	Y
Cresols	Y	Y	Y
Cyclohexanone	Y	N	Y
Ethyl acetate	Y	N	Y
Ethyl ether	Y	N	Y
Ethyl benzene	Y	N	Y
Isobutyl alcohol	Y	N	Y
Methanol	Y	N	Y
Methyl ethyl ketone	Y	N	Y
Methyl isobutyl ketone	Y	N	Y
Methylene chloride	Y	N	Y

(continued)

TABLE 14.3 (continued)

Constituent	Amenable to conventional biological treatment	Amenable to aqueous chemical treatment	Amenable to incineration
Nitrobenzene	Y		Y
Pyridine	Y		Y
Tetrachloroethylene			Y
Toluene	Y		Y
Trichloroethylene	NA	NA	Y
Trichloromono-fluoromethane	NA	NA	Y
Xylene	Y		Y
Other Solvents			
1,1,2-Trichloroethane	NA	NA	Y
1,2-Dichloropropane	Y		Y
1,3-Dichloropropene (cis and trans isomers)	Y		Y
1,4-Dioxane	NA	NA	Y
Acetonitrile	Y	Y	Y
Aniline	Y		Y
Benzene	Y		Y
Chloroform	Y		Y
Cyclohexane	Y		Y
Dichlorodifluoromethane			Y
Ethylene dichloride	NA		Y

(continued)

TABLE 14.3 (continued)

Constituent	Amenable to conventional biological treatment	Amenable to aqueous chemical treatment	Amenable to incineration
Furfural	Y		Y
Propylene glycol	Y		Y
Tetrahydrofuran			Y
o-dichlorobenzene	Y		Y
Other Low Molecular Weight Organic Compounds			
Acrolein	Y	Y	Y
Acrylic acid	Y	Y	Y
Allyl alcohol	Y	Y	Y
Allyl chloride	Y	Y	Y
Cumene	NA		Y
Dimethylamine	Y		Y
Epichlorohydrin	NA	NA	Y
Ethyl acrylate	Y		Y
Ethylene diamine	Y	Y	Y
Ethylenimine	Y		Y
Formaldehyde	Y		Y
Methyl Methacrylate	Y		Y

Y = Affirmative
N = Negative
NA = No information available.

The advantages and limitations of the treatment processes discussed in this document are summarized in Table 14.4. Incineration and other thermal destruction processes are discussed first in the table because of their general applicability to the treatment of solvent wastes. As noted by Blaney and others, incineration may well prove to be the ultimate disposal method, at least for solvent sludges for which solvent recovery is impractical. Incineration will also be the major method used to dispose of still bottoms following recovery operations. However, the extent to which incineration will be used for these difficult to treat wastes will depend to some extent on the technical and regulatory requirements that will be imposed on solidification/stabilization.

Some of the technologies discussed in Table 14.4 are not generally intended to be used as final treatment processes. Agitated thin film evaporation and distillation, for example, are concerned primarily with recovery/reuse. Others like wet air oxidation and chemical oxidations are pretreatment processes than can be used to make a waste amenable to a finishing step such as biological treatment.

Ultimately, the selection of a specific treatment system from the list of potentially applicable processes will depend on cost, availability, and site specific factors. These considerations are discussed below.

Availability of Potential Management Options

The availability of each component of a waste management system will affect its overall applicability. Existing available onsite treatment process capacity (e.g., wastewater treatment system, boiler), ancillary equipment, labor, physical space, and utilities will have a signigicant impact on the economic viability of a treatment system. Purchased equipment must be available in sizes and processing capabilities which meet the specific needs of the facility. Offsite disposal, recovery, and treatment facilities and companies purchasing saleable products must be located within a reasonable distance of the generator to minimize transport costs. In addition, they must have available capacity for the waste type and volume generated. Finally, time constraints may eliminate certain treatment processes from consideration as a result of anticipated delays in procurement, permitting, installation, or start-up.

TABLE 14.4. SUMMARY OF SOLVENT TREATMENT PROCESSES

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Incineration				
Liquid injection incineration	All pumpable liquids provided wastes can be blended to Btu level of 8500 Btu/lb. Some solids removal may be necessary to avoid plugging nozzles.	Estimated that over 219 units are in use. Most widely used incineration technology.	Excellent destruction efficiency (>99.99%). Blending can avoid problems associated with residuals, e.g., HCl.	TSP, possibly some PICs, and HCl if halogenated organics are fired. Only minor ash if solids removed in pretreatment processes.
Rotary kiln incineration	All wastes provided Btu level is maintained.	Over 40 units in service; most versatile for waste destruction.	Excellent destruction efficiency (>99.99%).	Requires APCDs. Residuals should be acceptable if charged properly.
Fluidized bed incineration	Liquids or nonbulky solids.	Nine units reportedly in operation-circulating bed units under development.	Excellent destruction efficiency (>99.99%).	As above.
Fixed/multiple hearths	Can handle a wide variety of wastes.	Approximately 70 units in use. Old technology for municipal waste combustion.	Performance may be marginal for hazardous wastes, particularly halogenated wastes.	As above.
Use As A Fuel				
Industrial kilns	Generally all wastes, but Btu level, chlorine content, and other impurity content may require blending to control charge characteristics and product quality.	Only a few units now burning hazardous waste.	Usually excellent destruction efficiency (>99.99%) because of long residence times and high temperatures.	Requires APCDs. Residuals should be acceptable.
High temperature industrial boilers	All pumpable fluids, but should blend halogenated organics. Solids removal particularly important to ensure stable burner operation.	Several units in use.	Most units tested have demonstrated high DRE (>99.99%).	Wastes must be blended to meet emission standards for TSP and HCl unless boilers equipped with APCDs.

(continued)

TABLE 14.4 (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Other Thermal Technologies				
Circulating bed combustor	Liquids or nonbulky solids.	Only one U.S. manufacturer. No units treating hazardous waste.	Manufacturer reports high efficiencies (99.99%).	Bed material additives can reduce HCl emissions. Residuals should be acceptable.
Molten glass incineration	Almost all wastes, provided moisture and metal impurity levels are within limitations.	Technology developed for glass manufacturing Not available yet as a hazardous waste unit.	No performance data available, but DREs should be high (99.99%).	Will need APC device for HCl and possibly PICs; solids retained (encapsulated) in molten glass.
Molten salt destruction	Not suitable for high (20%) ash content wastes.	Technology under development since 1969, but further development on hold.	Very high destruction efficiencies for organics (six nines for PCBs).	Needs some APC devices to collect material not retained in salt. Ash disposal may be a problem.
Furnace pyrolysis units	Most designs suitable for all wastes.	One pyrolysis unit RCRA permitted. Certain designs available commercially.	Very high destruction efficiencies possible (99.99%). Possibility of PIC formation.	TSP emissions lower than those from conventional combustion . Will need APC devices for HCl. Certain wastes may produce an unacceptable tarry residual.
Plasma arc pyrolysis	Present design suitable only for liquids.	Commercial design appears imminent, with future modifications planned for treatment of sludges and solids.	Efficiencies exceeded six nines in tests with solvents.	Requires APC devices for HCP and TSP, needs flare for H_2 and CO destruction.
Fluid wall advanced electric reactor	Suitable for all wastes if solids pretreated to ensure free flow.	Ready for commercial development. Test unit permitted under RCRA.	Efficiencies have exceeded six nines.	Requires APC devices for TSP and HCl; Chlorine removal may be required.
In situ vitrification	Technique for treating contaminated soils, could possibly be extended to slurries. Also use as solidification process.	Not commercial, further work planned.	No data available, but DREs of over six nines reported.	Off gas system needed to control emissions to air. Ash contained in vitrified soil.

(continued)

TABLE 14.4 (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Physical Treatment Methods				
Distillation	This is a process used to recover and separate solvents. Fractional distillation will require solids removal to avoid plugging columns.	Technology well developed and equipment available from many suppliers; widely practiced technology.	Separation depends upon reflux (99+ percent achievable). This is a recovery process.	Bottoms will usually contain levels of solvent in excess of 1,000 ppm; condensate may require further treatment.
Evaporation	Agitated thin film units can tolerate higher levels of solids and higher viscosities than other types of stills.	Technology is well developed and equipment is available from several suppliers; widely practices technology.	This is a solvent recovery process. Typical recovery of 60 to 70 percent.	Bottoms will contain appreciable solvent. Generally suitable for incineration.
Steam Stripping	A simple distillation process to remove volatile organics from aqueous solutions. Preferred for low concentrations and solvents with low solubilities.	Technology well developed and available.	Not generally considered a final treatment, but can achieve low residual solvent levels.	Aqueous treated stream will probably require polishing. Further concentration of overhead steam generally required.
Air Stripping	Generally used to treat low concentration aqueous streams.	Technology well developed and available.	Not generally considered a final treatment, but may be effective for highly volatile wastes.	Air emissions may require treatment.
Liquid-Liquid Extraction	Generally suitable only for liquids of low solid content.	Technology well developed for industrial processing.	Can achieve high efficiency separations for certain solvent/waste combinations.	Solvent solubility in aqueous phase should be monitored.
Carbon Adsorption	Suitable for low solid, low concentration aqueous waste streams.	Technology well developed; used as polishing treatment.	Can achieve low levels of residual solvent in effluent.	Adsorbate must be processed during regeneration. Spent carbon and wastewater may also need treatment.
Resin Adsorption	Suitable for low solid waste streams. Consider for recovery of valuable solvent.	Technology well developed in industry for special resin/solvent combinations. Applicability to waste streams not demonstrated.	Can achieve low levels of residual solvent in effluent.	Adsorbate must be processed during regeneration.

(continued)

TABLE 14.4 (Continued)

Process	Applicable waste streams	Stage of development	Performance	Residuals generated
Chemical Treatment Processes				
Wet air oxidation	Suitable for aqueous liquids, also possible for slurries. Solvent concentrations up to 15%.	High temperature/ pressure technology, widely used as pretreatment for municipal sludges, only one manufacturer.	Pretreatment for biological treatment. Some compounds resist oxidation.	Some residues likely which need further treatment.
Supercritical water oxidation	For liquids and slurries containing optimal concentrations of about 10% solvent.	Supercritical conditions may impose demands on system reliability. Commercially available in 1987.	Supercritical conditions achieve high destruction efficiencies (>99.99%) for all constituents.	Residuals not likely to be a problem. Halogens can be neutralized in process.
Ozonation	Oxidation with ozone (possibly assisted by (UV) suitable for low solid, dilute aqueous solutions.	Now used as a polishing step for wastewaters.	Not likely to achieve residual solvent levels in the low ppm range for most wastes.	Residual contamination likely; will require additional processing of off gases.
Other chemical oxidation processes	Oxidizing agents may be highly reactive for specific constituents in aqueous solution.	Oxidation technology well developed for cyanides and other species (phenols), not yet established for general utility.	Not likely to achieve residual solvent levels in the low ppm range for most wastes.	Residual contamination likely; will require additional processing.
Chlorinolysis	Suitable for any liquid chlorinated wastes.	Process produces a product (e.g., carbon tetrachloride). Not likely to be available	Not available.	Air and wastewater emissions were estimated as not significant.
Dechlorination	Dry soils and solids.	Not fully developed.	Destruction efficiency of over 99% reported for dioxin.	Residual contamination seems likely.
Biological Treatment Methods				
	Aerobic technology suitable for dilute wastes although some constituents will be resistant.	Conventional treatments have been used for years.	May be used as final treatment for specific wastes, may be pretreatment for resistant species.	Residual contamination likely; will usually require additional processing.

Management System Cost Estimation

The relative economic viability of candidate waste management systems will be the primary determinant of ultimate system selection. This must be evaluated on the basis of total system costs which includes the availability of onsite equipment, labor and utilities, net value of recovered products and treatment/disposal processing costs. Costs for a given management system will also be highly dependent on waste physical, chemical, and flow characteristics. Thus, real costs are very site specific and limit the usefulness of generalizations. The reader is referred to the sections on specific technologies (Sections 7.0 through 13.0) for data on costs and their variability with respect to flow and waste characteristics. Major cost centers which should be considered are summarized in Table 14.5.

Modeling System Performance and Pilot Scale Testing

Following this preliminary cost evaluation which will enable the generator to narrow his choice of waste management options, steps must be taken to further finalize the selection process. These could involve the use of mathematical models to predict design and operating requirements. However, models often sacrifice accuracy for convenience and are not always adequate for complex waste streams. Laboratory data, or pilot plant and full-scale data, may ultimately be needed to confirm predicted performance. In fact, some data may be needed as model inputs for predicting system behavior.

Processes which rely on Henry's Law Constant are a good example of the need for experimentally documented data. Removal efficiency approximations using Henry's Law Constant based on a ratio of pure compound vapor pressure to its solubility often overestimate stripping by as much as two order of magnitude.[2] However, if Henry's Law Constant is obtained experimentally using headspace analysis and batch stripping methods, it can be effectively used to estimate equilibrium partitioning behavior.

Many models are useful for predicting constituent behavior in separation processes. These models are based on thermodynamic equilibrium partitioning and may also include kinetic factors to establish separation performances. Perry's Chemical Engineers' Handbook and other Chemical Engineering textbooks

TABLE 14.5 MAJOR COST CENTERS FOR WASTE MANAGEMENT ALTERNATIVES

A. Credits

- Material/energy recovery resulting in decreased consumption of purchased raw materials
- Sales of waste products

B. Capital Costs*

- Processing equipment
- Ancillary equipment (storage tanks, pumps, piping)
- Pollution control equipment
- Vehicles
- Buildings, land
- Site preparation, installation, start-up

C. Operating and Maintenance Costs

- Overhead, operating, and maintenance labor
- Maintenance materials
- Utilities (electricity, fuel, water)
- Reagent materials
- Disposal, offsite recovery and waste brokering fees
- Transportation
- Taxes, insurance, regulatory compliance, and administration

D. Indirect Costs and Benefits

- Impacts on other facility operations; e.g., changes in product quality as a result of source reduction or use of recycled materials
- Use of processing equipment for mangement of other wastes

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*Annual costs derived by using a capital factor:

$$CRF = \frac{i(1+i)^n}{(1+i)^n-1}$$

Where: i = interest rate and n = life of the investment. A CRF of 0.177 was used to prepare cost estimates in this document. This corresponds to an annual interest rate of 12 percent and an equipment life of 10 years.

are sources of information about such models.[12-16] Standard analytical packages are also avialable to predict the fate of waste stream contaminants as they are exposed to unit operations such as stripping and distillation. For example, the Process^R Program developed by Simulation Sciences, Inc. was used recently to assess the fate of contaminants in waste oil as they flowed through a waste oil re-refining process. The Process^R Program allows simulation of most chemical separation processes for which the degree of completion is determined by thermodynamic equilibrium. The particular program used did not allow simulation of operations involving mass transfer and kinetics in addition to equilibrium. However, such programs are available and must be used when kinetic factors prevent thermodynamic equilibrium from being established; e.g., processing wastes with high viscosity and low solvent concentration.

In many cases models are useful in predicting behavior and can be used in place of costly laboratory testing. Models are also useful in assessing relative performance and costs of various approaches to treatments and the incremental costs of achieving increasingly stringent treatment concentration levels. Many suppliers of separation equipment use models to optimize design and operations parameters and to scale treatment processes. The use of models and other methods for assessing process performance are described in Perry's and techical articles, publications, and textbooks.

The need for experimental data will depend upon the complexity of waste stream/process interactions. Equipment manufacturers are often able to provide experimental equipment and models to establish process parameters and cost, including the costs required for disposal of residuals.

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APPENDIX A

PERTINENT PROPERTIES OF THE ORGANIC SOLVENTS AND OTHER LOW MOLECULAR WEIGHT ORGANICS

APPENDIX A

PROPERTIES OF THE ORGANIC SOLVENTS IN WASTE NUMBERS F001, F002, F004, AND F005

EXPLANATION OF SOME PROPERTIES DATA

The data presented in the Appendix A data sheets for the organic solvents in Classes F001, F002, F004, and F005 have been compiled from a variety of sources. A brief description of some of the properties data (as presented in the Treatability Manual (EPA-600/2-82-001a)) will clarify some of the information provided in the data sheets, including the units used, and explain the utility of individual parameters.

Henry's Law Constant

Henry's law constant is the relative equilibrium concentration of a compound in air and water at a constant temperature and is defined by the following equation:

$$K = \frac{P}{S}$$

where: K = Henry's law constant, m^3 atm mol^{-1}

P = compound's vapor pressure in atmospheres

S = compound's solubility in water in moles per cubic meter

The constant is an expression of the equilibrium distribution of a compound between air and water. The constant indicates qualitatively the volatility of a compound and is frequently used in equations that attempt to predict "stripping" of a compound from aqueous solution. Increasing values of the constant favor volatilization as a fate mechanism and indicate amenability to steam or air stripping.

Log Octanol/Water Partition Coefficient

The log octanol/water partition coefficient or log P is the equilibrium distribution of a compound between two immiscible solvents, n-octanol and water. It is defined by the following equation:

$$\text{Log } P = \text{Log } \frac{C_{A,O}}{C_{A,H_2O}}$$

where: $C_{A,O}$ = concentration of compound in n-octanol phase

C_{A,H_2O} = concentration of compound in water phase

Log P varies with temperature. The temperature of determination is assumed to be 25°C, although in many cases the temperature and method of determination are not known.

Log P measures the affinity of a compound for octanol and water phases. It is a useful parameter for predicting the bioconcentration potential of compounds and sorption of compounds by organic soils where experimental values are not available. It is also used to determine the applicability of solvent extraction as a treatment alternative. Increasing values favor strong bioaccumulation, adsorption, and solvent extraction potentials.

Carbon Adsorption Data

Batch equilibrium carbon adsorption isotherm data can be used to estimate the relative effectiveness of carbon in adsorbing organic compounds. The adsorption isotherm is the relationship, at a given temperature and other conditions, between the amounts of a substance adsorbed and its equilibrium concentrations remaining in solution.

Carbon adsorption data can be plotted according to the Freundlich equation. This is an empirical equation that is widely used and has been found to describe adequately the adsorption process in dilute solution. The Freundlich equation has the form:

$$\frac{X}{M} = KC_f^{1/m}$$

Data can be fitted to the logarithmic form of the above equation, which has the form:

$$\log \frac{X}{M} = \log K + 1/m \log C_f$$

where: $X = C_o - C_f$ = initial concentration of solute minus final concentration of solute in solution at equilibrium, mg/L

M = weight in grams of adsorbent (carbon) per liter

C_f = final concentration of solute in mg/L

K = intercept at $C_f = 1$ ($\log C_f = 0$)

$1/m$ = slope of the line

For dilute solutions in this study, this equation yields a straight line with a slope of 1/m and an intercept equal to the value of K when $C_f = 1$ ($\log C_f = 0$). The intercept is roughly an indicator of adsorption capacity and the slope, 1/m of adsorption intensity. The concentration of compound on the carbon in equilibrium with a concentration C_f is given by the X/M value, expressed as mg compound/gram of carbon.

The adsorbability is defined as the carbon dose required to reduce a pollutant concentration from concentration a to concentration b. The data here are reported for the reduction from 1 mg/L to 0.1 mg/L, to serve as a basis for comparing individual compounds.

Possible Treatment Methods

Possible treatment methods have not been provided in the data sheets. Incineration is a possible alternative for all, although a better definition of waste characteristics is needed to assess possible alternatives.

CHEMICAL NAME: Carbon tetrachloride

CAS NO.: 56-23-5

CHEMICAL FORMULA: CCl_4

RCRA ID: F001

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	153.82
MELTING POINT, °C:	-22.9
BOILING POINT, °C:	76.75
VAPOR PRESSURE, torr @ 20°C:	89.6
LIQUID DENSITY, g/ml @ 20°C:	1.59
VAPOR DENSITY (air = 1.0):	5.32
WATER SOLUBILITY, mg/l @ 20°C:	785
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.64
HENRY'S LAW CONSTANT, atm-m^3/mol:	3.02×10^{-2}
DIPOLE MOMENT, D:	0
DIELECTRIC CONSTANT @ 20°C:	2.24
FRACTIONAL POLARITY:	0.0
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	8.6
HEAT OF COMBUSTION, Kcal/mol:	37.3
HEAT OF VAPORIZATION, Kcal/mol:	7.63
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Probably occurs at an extremely slow rate.

PHYSIOCHEMICAL DEGRADATION: Oxidation is not a significant fate; hydrolysis and photolysis are too slow to be significant; volatilization is the primary transport process from the aquatic environment.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 11; 1/n = 0.83 Carbon dose = 550 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Chlorobenzene

CHEMICAL FORMULA: C_6H_5Cl

CAS NO.: 108-90-7

RCRA ID: F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	112.56
MELTING POINT, °C:	-45.6
BOILING POINT, °C:	132
VAPOR PRESSURE, torr @ 20°C:	8.8
LIQUID DENSITY, g/ml @ 20°C:	1.11
VAPOR DENSITY (air = 1.0):	3.88
WATER SOLUBILITY, mg/l @ 20°C:	488
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.84
HENRY'S LAW CONSTANT, atm-m^3/mol:	3.93×10^{-3}
DIPOLE MOMENT, D:	1.69
DIELECTRIC CONSTANT @ 20°C:	5.71
FRACTIONAL POLARITY:	0.058
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	9.5
HEAT OF COMBUSTION, Kcal/mol:	763.9
HEAT OF VAPORIZATION, Kcal/mol:	9.07
FLASH POINT, °C:	29

DEGRADATION

BIODEGRADATION: Probably will eventually biodegrade, but not at a substantial rate unless microbes present are already growing on another hydrocarbon source.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation in ambient waters; probably will not hydrolyze in ambient waters due to the extreme difficulty with which aryl halides undergo nucleophilic substitution; no information available on photolysis; probably volatilizes from water to the atmosphere at a relatively rapid rate.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 91; 1/n = 0.99 carbon dose = 92 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: m-cresol

CAS NO.: 108-39-4

CHEMICAL FORMULA: $CH_3C_6H_4OH$

RCRA ID: F004

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	108.15
MELTING POINT, °C:	11.5
BOILING POINT, °C:	202.2
VAPOR PRESSURE, torr @ 20°C:	0.04
LIQUID DENSITY, g/ml @ 20°C:	1.03
VAPOR DENSITY (air = 1.0):	3.72
WATER SOLUBILITY, mg/l @ 20°C:	23,500
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	1.96
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.4×10^{-6}
DIPOLE MOMENT, D:	1.54
DIELECTRIC CONSTANT @ 20°C:	11.8
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.2
HEAT OF COMBUSTION, Kcal/mol:	880.5
HEAT OF VAPORIZATION, Kcal/mol:	13.48
FLASH POINT, °C:	86

DEGRADATION

BIODEGRADATION: Readily iodegradable.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation; not known to hydrolize; no information on photolysis.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: o-cresol

CAS NO.: 95-48-7

CHEMICAL FORMULA: $CH_3C_6H_4OH$

RCRA ID: F004

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	108.15
MELTING POINT, °C:	30.9
BOILING POINT, °C:	191
VAPOR PRESSURE, torr @ 20°C:	0.24
LIQUID DENSITY, g/ml @ 20°C:	1.05
VAPOR DENSITY (air = 1.0):	3.72
WATER SOLUBILITY, mg/l @ 20°C:	25,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	1.95
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.4×10^{-6}
DIPOLE MOMENT, D:	1.41
DIELECTRIC CONSTANT @ 20°C:	11.5
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.2
HEAT OF COMBUSTION, Kcal/mol:	882.6
HEAT OF VAPORIZATION, Kcal/mol:	12.49
FLASH POINT, °C:	81

DEGRADATION

BIODEGRADATION: Readily biodegradable.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation; not known to hydrolize; some degradation by direct photolysis in aqueous media.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: p-cresol

CAS NO.: 106-44-5

CHEMICAL FORMULA: $CH_3C_6H_4OH$

RCRA ID: F004

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	108.15
MELTING POINT, °C:	34.8
BOILING POINT, °C:	201.9
VAPOR PRESSURE, torr @ 20°C:	0.11
LIQUID DENSITY, g/ml @ 20°C:	1.03
VAPOR DENSITY (air = 1.0):	3.72
WATER SOLUBILITY, mg/l @ 20°C:	24,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	1.94
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.4×10^{-6}
DIPOLE MOMENT, D:	1.54
DIELECTRIC CONSTANT @ 20°C:	9.9
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.2
HEAT OF COMBUSTION, Kcal/mol:	882.5
HEAT OF VAPORIZATION, Kcal/mol:	13.61
FLASH POINT, °C:	86

DEGRADATION

BIODEGRADATION: Readily biodegradable.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation; not known to hydrolize; no information on photolysis.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Cresylic acid

CAS NO.: 1319-77-3

CHEMICAL FORMULA: $CH_3C_6H_4OH$

RCRA ID: F004

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	108.15
MELTING POINT, °C:	10.9-35.5
BOILING POINT, °C:	195-205
VAPOR PRESSURE, torr @ 20°C:	0.24
LIQUID DENSITY, g/ml @ 20°C:	1.03-1.04
VAPOR DENSITY (air = 1.0):	3.72
WATER SOLUBILITY, mg/l @ 20°C:	25,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.04
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.4×10^{-6}
DIPOLE MOMENT, D:	1.5
DIELECTRIC CONSTANT @ 20°C:	10-12
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.2
HEAT OF COMBUSTION, Kcal/mol:	_880
HEAT OF VAPORIZATION, Kcal/mol:	_13
FLASH POINT, °C:	81

DEGRADATION

BIODEGRADATION: Similar to cresols.

PHYSIOCHEMICAL DEGRADATION:

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: o-Dichlorobenzene

CAS NO.: 95-50-1

CHEMICAL FORMULA: $C_6H_4CL_2$

RCRA ID: F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	147.00
MELTING POINT, °C:	-17.6
BOILING POINT, °C:	180.5
VAPOR PRESSURE, torr @ 20°C:	1
LIQUID DENSITY, g/ml @ 20°C:	1.30
VAPOR DENSITY (air = 1.0):	5.05
WATER SOLUBILITY, mg/l @ 20°C:	145
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	3.38
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.94 x 10^{-3}
DIPOLE MOMENT, D:	2.50
DIELECTRIC CONSTANT @ 20°C:	7.50
FRACTIONAL POLARITY:	0
SOLUBILITY PARAMETER, cal$^{0.5}$/cm$^{1.5}$:	10.0
HEAT OF COMBUSTION, Kcal/mol:	671.8
HEAT OF VAPORIZATION, Kcal/mol:	10.94
FLASH POINT, °C:	74

DEGRADATION

BIODEGRADATION: Sufficiently resistant to biodegradation to make volatilization more important.

PHYSIOCHEMICAL DEGRADATION: Resistant to autooxidation by peroxy radical in water; oxidation by hydroxyl radicals occurs in the atmosphere; hydrolysis is not important; photolysis probably occurs slowly.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 129; 1/n = 0.43 carbon dose = 19 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Isobutanol

CAS NO.: 78-83-1

CHEMICAL FORMULA: $(CH_3)_2CHCH_2OH$

RCRA ID: F005

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	74.12
MELTING POINT, °C:	-114.7
BOILING POINT, °C:	99.5
VAPOR PRESSURE, torr @ 20°C:	9
LIQUID DENSITY, g/ml @ 20°C:	0.81
VAPOR DENSITY (air = 1.0):	2.55
WATER SOLUBILITY, mg/l @ 20°C:	95,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	0.83
HENRY'S LAW CONSTANT, atm-m^3/mol:	2.2×10^6
DIPOLE MOMENT, D:	1.66
DIELECTRIC CONSTANT @ 20°C:	18.7
FRACTIONAL POLARITY:	0.11
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.7
HEAT OF COMBUSTION, Kcal/mol:	638.2
HEAT OF VAPORIZATION, Kcal/mol:	10.94
FLASH POINT, °C:	27

DEGRADATION

BIODEGRADATION: No information available.

PHYSIOCHEMICAL DEGRADATION: No information available for oxidation, hydrolysis, or photolysis.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Methylene chloride

CAS NO.: 75-09-2

CHEMICAL FORMULA: CH_2Cl_2

RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	84.94
MELTING POINT, °C:	-95
BOILING POINT, °C:	39.75
VAPOR PRESSURE, torr @ 20°C:	362.4
LIQUID DENSITY, g/ml @ 20°C:	1.33
VAPOR DENSITY (air = 1.0):	2.93
WATER SOLUBILITY, mg/l @ 20°C:	20,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	1.25
HENRY'S LAW CONSTANT, atm-m^3/mol:	3.19×10^{-3}
DIPOLE MOMENT, D:	1.60
DIELECTRIC CONSTANT @ 20°C:	9.08
FRACTIONAL POLARITY:	0.12
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	9.7
HEAT OF COMBUSTION, Kcal/mol:	106.8
HEAT OF VAPORIZATION, Kcal/mol:	7.57
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Probably occurs, but at an extremely slow rate.

PHYSIOCHEMICAL DEGRADATION: Oxidation in aqueous phase probably not important; hydrolysis probably not significant, neither are photochemical reactions in aqueous media. Volatilization is major pathway for loss from water.

ADDITIONAL INFORMATION

CARBON ADSORPTION: Ks 1.3; 1/n = 1.2 Carbon dose = 10,000 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Methyl ethyl ketone

CAS NO.: 78-93-3

CHEMICAL FORMULA: $CH_3COC_2H_5$

RCRA ID: F005

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	72.11
MELTING POINT, °C:	-86.35
BOILING POINT, °C:	79.64
VAPOR PRESSURE, torr @ 20°C:	71.2
LIQUID DENSITY, g/ml @ 20°C:	0.81
VAPOR DENSITY (air = 1.0):	2.5
WATER SOLUBILITY, mg/l @ 20°C:	100,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	0
HENRY'S LAW CONSTANT, atm-m^3/mol:	4.35×10^{-5}
DIPOLE MOMENT, D:	2.7
DIELECTRIC CONSTANT @ 20°C:	18.5
FRACTIONAL POLARITY:	0.510
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	9.3
HEAT OF COMBUSTION, Kcal/mol:	582.3
HEAT OF VAPORIZATION, Kcal/mol:	8.15
FLASH POINT, °C:	-1

DEGRADATION

BIODEGRADATION: Biodegradable.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation, hydrolysis, or photolysis.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Nitrobenzene CAS NO.: 98-95-3

CHEMICAL FORMULA: $C_6H_5NO_2$ RCRA ID: F004

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	123.11
MELTING POINT, °C:	-5.6
BOILING POINT, °C:	211
VAPOR PRESSURE, torr @ 20°C:	0.15
LIQUID DENSITY, g/ml @ 20°C:	1.2
VAPOR DENSITY (air = 1.0):	4.2
WATER SOLUBILITY, mg/l @ 20°C:	1,900
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	1.85
HENRY'S LAW CONSTANT, atm-m^3/mol:	2.4×10^{-5}
DIPOLE MOMENT, D:	4.22
DIELECTRIC CONSTANT @ 20°C:	35.74
FRACTIONAL POLARITY:	0.63
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.0
HEAT OF COMBUSTION, Kcal/mol:	739.2
HEAT OF VAPORIZATION, Kcal/mol:	12.17
FLASH POINT, °C:	88

DEGRADATION

BIODEGRADATION: Slow, but could be significant in the absence of appreciable photolysis.

PHYSIOCHEMICAL DEGRADATION: Oxidation is highly improbable; it is not known to hydrolize; photolysis may be significant if the compound is adsorbed on humus near the air/water surface. Volatilization is unlikely to be significant in transport.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 68; 1/n = 0.43 carbon dose = 36 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME:	Pyridine	CAS NO.:	110-86-1
CHEMICAL FORMULA:	$CH < (CHCH)_2 > N$	RCRA ID:	F005

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	79.10
MELTING POINT, °C:	-42
BOILING POINT, °C:	115.3
VAPOR PRESSURE, torr @ 20°C:	20
LIQUID DENSITY, g/ml @ 20°C:	0.98
VAPOR DENSITY (air = 1.0):	2.73
WATER SOLUBILITY, mg/l @ 20°C:	Miscible
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	0.64
HENRY'S LAW CONSTANT, $atm\text{-}m^3/mol$:	2.4×10^{-5}
DIPOLE MOMENT, D:	2.19
DIELECTRIC CONSTANT @ 20°C:	12.5
FRACTIONAL POLARITY:	0.174
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	10.7
HEAT OF COMBUSTION, Kcal/mol:	658.5
HEAT OF VAPORIZATION, Kcal/mol:	9.65
FLASH POINT, °C:	23

DEGRADATION

BIODEGRADATION: Likely to be persistent in the abiotic environment of most ground waters.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation, hydrolysis, or photolysis.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Tetrachloroethylene

CAS NO.: 127-18-4

CHEMICAL FORMULA: $Cl_2C:CCl_2$

RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	165.85
MELTING POINT, °C:	-22.7
BOILING POINT, °C:	121
VAPOR PRESSURE, torr @ 20°C:	14
LIQUID DENSITY, g/ml @ 20°C:	1.63
VAPOR DENSITY (air = 1.0):	5.8
WATER SOLUBILITY, mg/l @ 20°C:	150
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.88
HENRY'S LAW CONSTANT, atm-m^3/mol:	2.82×10^{-2}
DIPOLE MOMENT, D:	1.32
DIELECTRIC CONSTANT @ 20°C:	2.46
FRACTIONAL POLARITY:	0
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	9.35
HEAT OF COMBUSTION, Kcal/mol:	162.5
HEAT OF VAPORIZATION, Kcal/mol:	9.24
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Potentially biodegradable; probably slow; conflicting results.

PHYSIOCHEMICAL DEGRADATION: Oxidation occurs slowly in aquatic environment; hydrolysis is probably too slow to be significant; photolysis probably does not occur; volatilization is the primary transport process.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 51; 1/n = 0.56 carbon dose = 64 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME:	Toluene	CAS NO.:	108-88-3
CHEMICAL FORMULA:	$C_6H_5CH_3$	RCRA ID:	F005

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	92.13
MELTING POINT, °C:	-95
BOILING POINT, °C:	110.6
VAPOR PRESSURE, torr @ 20°C:	28.4
LIQUID DENSITY, g/ml @ 20°C:	0.87
VAPOR DENSITY (air = 1.0):	3.14
WATER SOLUBILITY, mg/l @ 20°C:	470
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.69
HENRY'S LAW CONSTANT, atm-m^3/mol:	5.93×10^{-3}
DIPOLE MOMENT, D:	0.36
DIELECTRIC CONSTANT @ 20°C:	2.39
FRACTIONAL POLARITY:	0.001
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	8.9
HEAT OF COMBUSTION, Kcal/mol:	934.2
HEAT OF VAPORIZATION, Kcal/mol:	8.58
FLASH POINT, °C:	7

DEGRADATION

BIODEGRADATION: Relative importance of biodegradation cannot be determined.

PHYSIOCHEMICAL DEGRADATION: Oxidation is probably not important as aquatic fate; atmospheric photo-oxidation subordinates all other fate processes. Hydrolysis not aquatically significant; volatilization is significant transport process.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 26; 1/n = 0.44 carbon dose = 96 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: 1,1,1-Trichloroethane

CHEMICAL FORMULA: Cl_3CCH_3

CAS NO.: 71-55-6

RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	133.41
MELTING POINT, °C:	-30.41
BOILING POINT, °C:	74.1
VAPOR PRESSURE, torr @ 20°C:	96.0
LIQUID DENSITY, g/ml @ 20°C:	1.34
VAPOR DENSITY (air = 1.0):	4.6
WATER SOLUBILITY, mg/l @ 20°C:	950
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.17
HENRY'S LAW CONSTANT, atm-m^3/mol:	4.92×10^{-3}
DIPOLE MOMENT, D:	1.78
DIELECTRIC CONSTANT @ 20°C:	7.5
FRACTIONAL POLARITY:	0.069
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	8.5
HEAT OF COMBUSTION, Kcal/mol:	213.3
HEAT OF VAPORIZATION, Kcal/mol:	8.01
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Probably occurs, but at an extremely slow rate.

PHYSIOCHEMICAL DEGRADATION: Oxidation not significant; hydrolysis probably too slow to be significant; photolysis not significant; volatilization is primary transport process in aquatic environment.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 2.48; 1/n = 0.34 carbon dose = 800 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Trichloroethylene

CAS NO.: 79-01-6

CHEMICAL FORMULA: $Cl_2C{:}CHCl$

RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	131.39
MELTING POINT, °C:	-73
BOILING POINT, °C:	87.19
VAPOR PRESSURE, torr @ 20°C:	57.9
LIQUID DENSITY, g/ml @ 20°C:	1.94
VAPOR DENSITY (air = 1.0):	4.53
WATER SOLUBILITY, mg/l @ 20°C:	1,000
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.29
HENRY'S LAW CONSTANT, atm-m^3/mol:	1.17×10^{-2}
DIPOLE MOMENT, D:	0.8
DIELECTRIC CONSTANT @ 20°C:	3.42
FRACTIONAL POLARITY:	0.005
SOLUBILITY PARAMETER, cal$^{0.5}$/cm$^{1.5}$:	9.2
HEAT OF COMBUSTION, Kcal/mol:	230.0
HEAT OF VAPORIZATION, Kcal/mol:	8.32
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Potentially biodegradable; probably slow; conflicting results.

PHYSIOCHEMICAL DEGRADATION: Oxidation occurs slowly in aquatic environment; hydrolysis is probably too slow to be significant; photolysis probably does not occur; volatilization is the primary transport process.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 28; 1/n = 0.62 carbon dose = 130 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: Trichlorofluoromethane

CAS NO.: 75-69-4

CHEMICAL FORMULA: CCl_3F

RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	137.4
MELTING POINT, °C:	-111
BOILING POINT, °C:	23.8
VAPOR PRESSURE, torr @ 20°C:	667.4
LIQUID DENSITY, g/ml @ 20°C:	1.5
VAPOR DENSITY (air = 1.0):	4.7
WATER SOLUBILITY, mg/l @ 20°C:	1,125
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.53
HENRY'S LAW CONSTANT, atm-m^3/mol:	5.83×10^{-2}
DIPOLE MOMENT, D:	0.45
DIELECTRIC CONSTANT @ 20°C:	2.41
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	8.0
HEAT OF COMBUSTION, Kcal/mol:	-
HEAT OF VAPORIZATION, Kcal/mol:	6.42
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: Volatility probably precludes biodegradation.

PHYSIOCHEMICAL DEGRADATION: Oxidation not a significant fate; hydrolysis too slow to be significant; photolysis not significant; volatilization is primary transport process.

ADDITIONAL INFORMATION

CARBON ADSORPTION: K = 5.6; 1/n = 0.24 carbon dose = 280 mg/l

POSSIBLE TREATMENT METHODS:

CHEMICAL NAME: 1,1,2-Trichloro-1,2,2-trifluoroethane CAS NO.: 76-13-1

CHEMICAL FORMULA: FCl_2CCClF_2 RCRA ID: F001, F002

CHEMICAL/PHYSICAL PROPERTIES

MOLECULAR WEIGHT:	187.38
MELTING POINT, °C:	-36.4
BOILING POINT, °C:	48
VAPOR PRESSURE, torr @ 20°C:	270
LIQUID DENSITY, g/ml @ 20°C:	1.56
VAPOR DENSITY (air = 1.0):	6.5
WATER SOLUBILITY, mg/l @ 20°C:	10
LOG OCTANOL/WATER COEFFICIENT, $K_{o/w}$:	2.00
HENRY'S LAW CONSTANT, atm-m^3/mol:	4.3×10^{-2}
DIPOLE MOMENT, D:	-
DIELECTRIC CONSTANT @ 20°C:	2.41
FRACTIONAL POLARITY:	-
SOLUBILITY PARAMETER, $cal^{0.5}/cm^{1.5}$:	7.4
HEAT OF COMBUSTION, Kcal/mol:	-
HEAT OF VAPORIZATION, Kcal/mol:	7.12
FLASH POINT, °C:	None

DEGRADATION

BIODEGRADATION: No information available.

PHYSIOCHEMICAL DEGRADATION: No information available on oxidation, hydrolysis, or photolysis. Volatilization is most important transport mechanism.

ADDITIONAL INFORMATION

CARBON ADSORPTION:

POSSIBLE TREATMENT METHODS:

TABLE A-1. PHYSICAL AND CHEMICAL PROPERTIES OF SOLVENTS AND OTHER LOW MOLECULAR WEIGHT ORGANICS.

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Solvents of Concern													
1,1,1-trichloroethane	U226	$C_2H_3Cl_3$	133.4	74.1	125	720	382	1.33	0.03	320, 309	1,110	None	33.5
1,1,2-trichloro-1,2,2-trifluoroethane	Z049	$CFCl_2CF_2Cl$	187.38	48	270^{20} 400^{30}	NA	NA	1.56	0.482	436.5	NA	None	29.77
1,2,-dichlorobenzene	U071	$C_6H_4Cl_2$	147.01	173	2.28	123	NA	1.28	$1.94x10^{-3}$	$3.6x10^3$ $2.4x10^3$	673	63	43.71
1-butanol	U031	$CH_3(CH_2)_3OH$	74	117.25	6.5	91,000	42.9	0.81	$7x10^{-6}$ $8.9x10^{-6}$	7.58	2,675	36-38	45.9
Acetone	U002	CH_3COCH_3	58	56.2	200 266	miscible	24.6	0.79	$6.8x10^{-6}$ $2.5x10^{-5}$	0.58	1,790	-18 (CC)	31.97
Carbon Disulfide	P022	CS_2	76	46.25	357	2,940	1	1.263	0.015	69.2 144.5	1,031	-30 (CC)	28.40
Carbon Tetrachloride	U211	CCl_4	153.82	76.54	113	1,160	NA	1.594	0.023	912 436	156	None	34.6 31.9
Chlorobenzene	U037	C_6H_5Cl	112.56	132	11.7^{20}	488	10,500	1.106	$3.93x10^{-3}$	765	3,108	23	40.3
Cresols	U052	$C_6H_4CH_3OH$	108	o: 192 m: 202.8 p: 201.9	o: 0.43 m: 0.18 p: 0.16	o: 31,000 m: 23,500 p: 24,000	209	o: 1.041 m: 1.038 p: 1.034	o: $2x10^{-6}$ m: $1x10^{-6}$ p: $9.5x10^{-7}$	m: 91.2 102.3 p: 83.2 87.2	o: 369 m: 368 p: 369	o: 81-83 m: 86 (CC) p: 86 (CC)	o: 52.25 m: 56.42 p: 56.95
Cyclohexanone	U057	$C_6H_{10}O$	98	156	4.57	23,000	236	0.95	$2.56x10^{-5}$ $4.1x10^{-6}$	6.46	NA	63 (CC)	42.0
Ethyl acetate	U112	$CH_3COOC_2H_5$	88	77	82.2 85	79,000	105	0.90	$5.76x10^{-5}$ $1.28x10^{-4}$	4.57 5.37	2,246	7.2 (OC)	34.73
Ethyl ether	U117	$C_2H_5OC_2H_5$	74	34.51	540	60,500	NA	0.713	$8.69x10^{-4}$	5.89 6.76	2,727	45 (CC)	29.06
Ethyl benzene	Z048	$C_6H_5C_2H_5$	106.16	136.25	10	140^{15}	27,000	0.866	$8.7x10^{-3}$	1,412	4,565	18 (CC)	38.92
Isobutyl alchohol	U140	$(CH_3)_2CHCH_2OH$	74	99.5	10 12	95,000	43	0.798	$1.03x10^{-5}$ $2.2x10^{-6}$	4.47 6.76	2,670	27.8	45.76

(continued)

TABLE A-1 (continued)

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Methanol	U154	CH_3OH	32	65	113.9	Miscible	1.53	0.796^{15}	1.1×10^{-6} 2.7×10^{-6}	0.15 0.22	726	12 (CC)	39.23 37.57
Methyl ethyl ketone	U159	$CH_3COCH_2CH_3$	72.1	79.6	100	2.70×10^{5}	58	0.805	4.35×10^{-5}	1.82	2,444	1.7	34.10
Methyl isobutyl ketone	U161	$(CH_3)_2CHCH_2$ $COCH_3$	100	117-119	7.5	$17{,}000^{20}$	794	0.801	5.41×10^{-5}	NA	NA	20	NA
Methylene chloride	U080	CH_2Cl_2	84.93	40	349^{20} 500^{30}		95.06	1.326	3.19×10^{-3}	18.2 17.8	604.6	None	31.7
Nitrobenzene	U169	$C_6H_5NO_2$	123	210.8	0.209	1,900	2,958	1.20^{25}	2.4×10^{-5} 1.3×10^{-5}	70.8 75.8	3,092	88 (CC)	50.91
Pyridine	U196 P075	C_5H_5N	79	115.5	20	Miscible	1,622	0.982	7×10^{-9} 2.36×10^{-5}	4.36 10.96	2,782	75 (CC)	40.37
Tetrachloroethylene	U210	C_2Cl_4	165.83	121	14^{20}	200^{20}	382	1.623	0.0153 28.7×10^{-3}	759, 400	825	Non-flammable	38.66
Toluene	U220	C_7H_8	92.18	110.6	28.7	534.8	11,100 114	0.867	6.66×10^{-3}	620, 537	3,908	4	39.2 35.9
Trichloroethylene	U228	C_2HCl_3	131.39	87	90	1000^{20}	382	1.464	9.1×10^{-3} 11.7×10^{-3}	263, 194	956	None	34.79
Thrichloromonofluoromethane	U121	CCl_3F	137	23.7	768 796	1,100	1	1.56	5.83×10^{-2}	339	NA	None	26.88
Xylene	U239	$C_6H_4(CH_3)_2$	106	o: 144.4 m: 139 p: 138.4	o: 2.77 m: 3.20 p: 3.15	175	15,188	o: 0.880 m: 0.871 p: 0.861	o: 5.27×10^{-3} m: 2.55×10^{-3} p: 2.51×10^{-3}	o: 588.8 m: 1584.9 p: 1412.5	o: 4567 m: 4553 p: 4556	o: 17 (CC) m: 25 (CC) p: 25 (CC)	o: 41.83 m: 41.44 p: 41.04

(continued)

TABLE A-1 (continued)

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Other Solvents													
1,1,1,2-Tetrachloroethane	U208	$C_2H_2Cl_4$	167.85	130 138	13.9	200^{20}	382	1.54	0.011	1100	976	None	38.9 36.5
1,1,2,2-Tetrachloroethane	U209	$C_2H_2Cl_4$	167.85	146.2	5.9 9	2,900^{20}	382	1.59	3.8x10^{-4}	245, 363	976	None	41.49
1,1,2-Trichloroethane	U227	$C_2H_3Cl_3$	133.41	113.8	24.8	4,500^{20} 1,000^{25}	382	1.44	7.42x10^{-4}	117, 148	1110	None	38.3
1,1-Dichloroethylene	U078	CH_2CCl_2	97	31.9	630 600	3,200 400	382	1.218	1.5x10^{-2} 1.91x10^{-1}	NA	NA	-17.8 (OC)	30.17
1,2-Dichloroethylene, trans isomer	U079	$C_2H_2Cl_2$	96.94	47.5	318	600^{20}	382	1.256	5.32x10^{-3}	3.4x10^2	1217	2	30.30
1,2-Dichloropropane	U083	$C_3H_6Cl_2$	112.99	96.4	49.6	2,700^{20}	NA	1.156	2.31x10^{-3}	105, 191	1886	4, 16	35.26
1,3-Dichloropropene (cis and trans isomers)	U084	$C_3H_4Cl_2$	110.97	104.3 (cis) 112 (trans)	25^{20}	2,700-2,800	NA	1.217 (cis) 1.224 (trans)	1.33x10^{-3}	100, 95.5	1597	27,35 (both isomers)	NA
1,4-Dichloro-2-butene	U074	$C_4H_4Cl_2$	125	154,158	4.0	9.701	NA	1.183^{25}	6.78x10^{-5}	NA	NA	NA	NA
1,4-Dioxane	U108	$C_4H_8O_2$	88	101	37	6x10^7	96.6	1.033	7.14x10^{-7}	0.38	2431	5 to 18	35.65
2-Ethoxy ethanol	U359	$HO(CH_2)_2OC_2H_5$	90.12	135	3.8^{20} 7^{30}	Soluble	NA	0.931	NA	0.288	NA	44 (CC) 49 (OC)	NA
2-Nitropropane	U171	$C_3H_7NO_2$	89	120	17.5	17	NA	.992	0.121	NA	1999	24	39.65
2-Picoline	U191	$C_5H_4NCH_3$	93	128.8	10	51,000	2,181	0.95^{15}	2.4x10^{-5}	11.48	NA	38.9	41.56
Acetonitrile	U003	CH_3CN	41	81.6	100	2.2x10^6 8.4x10^5	10.89	0.79	2.47x10^{-6} 5.8x10^{-6}	0.46	1,265	12.8	34.20
Aniline	U012	$C_6H_5NH_2$	93	184	0.85 0.75	34,000	94	1.02	3.07x10^{-6} 2.6x10^{-6}	7.94 9.55	3,396	76 (CC)	47.31
Benzene	U019	C_6H_6	78.12	80.1	74	1780	2,080	0.876	5.5x10^{-3}	135	3,267	-11	34.085 42.903

(continued)

TABLE A-1 (continued)

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Bis (chloromethyl) ether	P016	$C_2H_4Cl_2O$	114.96	104	30^{20}	22,000	7.9	1.315	2.1×10^{-4}	2.4	947	31	NA
Bromoform	U225	$CHBr_3$	253.38	149.5	5.6	3,190	NA	2.89	5.32×10^{-4}	199.5	138	None	40.47
Chloroform	U044	$CHCl_3$	119	61.7	160^{20} 200	7,800	95	1.483	3.39×10^{-3}	93	373	None	31.38
Cyclohexane	U056	C_6H_{12}	84	81	77^{20} 120^{30}	55	NA	0.779	0.178	NA	3,919	-18 (CC)	32.76
Dichlorodifluoromethane	U075	CCl_2F_2	120.92	-29.8	4,830	280	NA	1.329	2.75 0.40	NA	NA	NA	26.30
Ethyl carbamate	U238	$C_3H_7NO_2$	89.11	184	0.36	9.6×10^6 2×10^6	NA	0.986	2×10^{-8}	NA	NA	NA	NA
Ethylene dichloride	U077	$C_2H_4Cl_2$	98.96	83.5	80.4	8,700	382	1.235	9.14×10^{-4}	30	1,418	13	33.3
Ethylidene dichloride	U076	$C_2H_4Cl_2$	98.96	57.3	234	1,000	382	1.175	4.26×10^{-3}	63	1,242	-6	30.2
Furan	U124	C_4H_4O	68	31.36	634 596	10,000	NA	0.937	5.7×10^{-3}	NA	2,092	-35 (CC)	27.17
Furfural	U125	C_4H_3OCHO	96	161.7	53	83,000	NA	1.16	3.6×10^{-6} 8.10×10^{-5}	NA	2,340	60 (CC) 68 (CC)	NA
Hexachloroethane	U131	C_2Cl_6	236.74	186 @ 777 mm Hg	0.4^{20} 0.8^{30}	50^{22}	382	2.82	2.49×10^{-3}	4.2×10^4 2.4×10^3	460	None	49.0
Propylene glycol	P100	$CH_3CHOHCH_2OH$	76.1	188.2	0.2^{20}	Miscible	NA	1.038	NA	0.045	1,803	99 (OC)	56.80
Tetrahydrofuran	U213	C_4H_8O	72	67	149 72	1.4×10^5 1.31×10^5	NA	0.888	1.08×10^{-4} 4.9×10^{-3}	NA	2502	-17.2	NA
o-dichlorobenzene	U070	$C_6H_4Cl_2$	147.01	180.5	1.5	145	52,500	1.305	1.93×10^{-3}	3.6×10^3 2.3×10^3	2,810	66.1	45.79

(continued)

TABLE A-1 (continued)

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Ignitables													
1-Methylbutadiene	U186	C_5H_8	68	42	414	870	NA	NA	0.0424	NA	NA	-42.8	NA
2,2'-Bioxirane	U085	$CH_2(CH)_3O_2$	86.09	144	7.5	$8.3x10^7$	NA	NA	$1.02x10^{-8}$	NA	NA	NA	NA
2-Methylaziridine	P067	C_3H_7N	57.11	20	92.0	$3.1x10^6$	NA	NA	$2.22x10^{-5}$	NA	NA	-10	NA
Acrolein	P003	CH_2CHCHO	56	53	258	280,000	NA	0.842	$6.79x10^{-5}$	NA	1,630	-18 (OC)	31.92
Acrylic acid	U008	$CH_2CHCOOH$	72.06	141	3.2^{20}	$3.5x10^5$	10.7	1.06^{16}	$1x10^{-7}$	2.04-2.69	1,368	68 (OC)	45.84
Allyl alcohol	P005	CH_2CHCH_2OH	58.09	96-97	28.1	62,000	NA	0.854	$3.47x10^{-6}$	NA	1,851	21 (CC)	44.26
Allyl chloride	Z010	CH_2CHCH_2Cl	76.53	44-45	340^{20} 440^{30}	100	NA	0.938	NA	NA	NA	-31 (CC)	30.91
Chloroacetaldehyde	P023	C_2H_3ClO	78.50	86	100^{20}	Soluble	4.2	1.19^{25}	10^{-3}	0.42	959	17	NA
Chloromethyl methyl ether	U046	CH_3OCH_2Cl	81	59.5	214	$2.5x10^6$	NA	1.061	$9.12x10^{-6}$	NA	NA	NA	NA
Chloroprene	X009	$CH_2CClCHCH_2$	88.54	59.4	215.4	Slightly soluble	NA	0.958	NA	NA	NA	-20	NA
Cumene	U055	C_9H_{12}	120.19	152.7	4.6	50^{20}	45,082	0.862	0.0146	4,571	5,218	39 (CC)	43.24
Dimethylamine	U092	$(CH_3)_2NH$	45.08	7.4	1,500	Very soluble	1	0.68^0	$6.83x10^{-4}$	0.42, 0.95	1,743	-92.19	27.86
Dipropylamine	U110	$(C_3H_7)_2NH$	101.2	109-111	30	12,000	NA	0.738	$3.32x10^{-4}$	53.7	NA	17.2 (OC)	NA
Epichlorohydrin	U041	C_3H_5ClO	92.53	116.5	12^{20} 22^{30}	66,000 $60,000^{20}$	NA	1.180	$3.13x10^{-5}$	0.42	1,770	32 (OC)	174
Ethanal	U001	CH_3CHO	44.1	20.2	916	$5.6x10^5$	15.6	0.783^{18}	$9.5x10^{-5}$	2.69	1,166	-38 (CC)	30.41
Ethyl acrylate	U113	$CH_2CHCOOC_2H_5$	100.11	100	40	20,000 15,000	414	0.924	$3.5x10^{-4}$	NA	2,742	15 (OC)	38.74
Ethylene diamine	P053	$NH_2CH_2CH_2NH_2$ (H_2O)	78.1 hydrate 60.1 anhydrous	118 hydrate	116^{10} anhydrous 9^{20} hydrate		NA	0.963 hydrous 0.8994 anhydrous	NA	NA	1,893	43 (CC)	41.99 *

(continued)

TABLE A-1 (continued)

Constituent	EPA code	Chemical formula	Molecular weight (g/M)	Boiling point (°C)	Vapor pressure (mm Hg @ 25°C)*	Solubility in water (mg/L @ 25°C)*	Activity coefficient	Specific gravity (@ 20/4°C)*	Henry's Law constant (atm m^3 mol^{-1})	Octanol-water partition coefficient	Heat of combustion (KJ/mole @ 25°C)*	Flash point (°C)**	Heat of vaporization (KJ/mole @ 25°C)*
Ethylenimine	P054	C_2H_5N	43.07	56	200	Miscible	NA	0.832	$1.1x10^{-5}$	NA	NA	NA	NA
Ethylmethacrylate	U118	NA	114	117	19	19,000	NA	NA	$1.49x10^{-4}$	NA	NA	NA	NA
Formaldehyde	U122	CH_2O	30.03	-21 -79.6@20mm Hg	$760^{-19.5}$	Miscible	1.46	0.815	$5.1x10^{-4}$	0.13	570	56	24.76
Glycidylaldehyde	U126	$CHOCHOCH_2$	72	97	42.6	Very soluble	NA	NA	$5.8x10^{-7}$	NA	NA	NA	NA
Methacrylonitrile	U152	$CH_2C(CH_3)CN$	67.09	90.3	65	16	144	0.800	0.392	NA	NA	13 (OC)	33.82
Methyl bromide	U029	CH_3Br	95	3.56	5,300	900	NA	1.730^{0}	$5.26x10^{-3}$	NA	770	None	24.79
Methyl chloride	U045	CH_3Cl	50.49	-24.2	$3,800^{20}$ $5,092^{30}$	$6.27x10^{3}$	95.06	0.916	0.04 $8.14x10^{-3}$	8.9	687	0	22.5
Methyl chlorocarbonate	U156	$C_2H_3ClO_2$	94.50	71	113	Slightly soluble	NA	NA	NA	NA	NA	12	NA
Methyl methacrylate	U162	$CH_2C(CH_3)COOCH_3$	100.11	101	40	$7.8x10^{4}$	161	0.936	$6.6x10^{-5}$	NA	NA	NA	37.55
Oxirane	U115	C_2H_4O	44.05	11	1,294	Very soluble	NA	0.887	$3.63x10^{-5}$	NA	1,264	-20	28.55
Paraldehyde	U182	$C_6H_{12}O_3$	132.16	128	25.3^{20}	$120,000^{13}$	NA	0.994	$3.7x10^{5}$	2	3,483	35.6 (OC)	NA
Thiomethanol	U153	CH_3SH	48.11	6.2	1520	23,200	NA	0.868	$4x10^{-3}$	NA	NA	-18	26.49
n-Propylamine	U194	$CH_3CH_2CH_2NH_2$	59.11	49	245^{20}	Miscible	NA	0.718	$2.0x10^{-5}$	1.41, 2.34	2,365	-12 (CC)	31.0

*Temperature in °C otherwise noted as a superscript.

**CC = Closed Cup, OC = Open Cup.

APPENDIX B

MANUFACTURER PROFILES:
SOLVENT DISTILLATION EQUIPMENT

Source: Naval Energy and Environmental Support Activity, NEESA 20.3-013. Assessment of Solvent Distillation Equipment, Appendix A. December 1985.

MANUFACTURER PROFILES

(1) Alternative Resource Management Inc.
P. O. Box 1265
Miami, Oklahoma 74355
(918) 540-2511

Still Type: Continuous feed

Solvents Designed For: Explosion-proofing and vacuum attachments are optional. Therefore, depending upon the still obtained, any solvent (flammable or nonflammable) with a boiling point up to 500°F can be distilled. Standard models operate at atmospheric pressure and are not explosion-proof and, therefore, can distill nonflammable (halogenated) solvents with boiling points up to approximately 350°F.

Water Separator: Optional

Thruput/Capacity: ARM can build stills with thruputs ranging from 5 to 200 GPH.

Materials of Construction: Stainless steel construction is available as an option.

Safety Features: Vapor temperature and boiler temperature thermostats are standard. Liquid level controls and an automatic feed pump is also standard. A condenser flow switch turns the unit off if there is a lack of cooling water.

Heating and Cooling Options: Standard models are heated by a steam jacket. Electrical heating is optional.

Utility Requirements: 440-480V 3-phase power is required as well as cooling water, drainage, and compressed air to run pumps.

Available Models: Specifications and base prices for ARM's standard solvent stills are listed in Table A-1. Explosion proofing, vacuum attachments, water separators, and stainless steel construction are all optional and will raise the prices accordingly. Stills larger than those listed are available, but must be custom designed and built.

TABLE A-1
A.R.M. STILLS

MODEL	THRUPUT	PRICE
5	5 GPH	$ 4,800
15	15 GPH	$10,200
25	25 GPH	$24,600
50	50 GPH	$43,850

(2) Baron-Blakeslee, Inc.
2001 North Janice Avenue
Melrose Park, Illinois 60160.
(312) 450-3900

Still Type: Continuous feed

Solvents Designed For: The stills are not explosion proof and they operate at atmospheric pressure (no vacuum available). Therefore, they can distill only nonflammable (halogenated) solvents with a boiling point below approximately 350°F. Units are designed specifically for either chlorinated solvents or "Freons".

Water Separator: Standard

Thruput/Capacity: The stills are generally large (60-300 GPH for chlorinateds, 10-1200 GPH for "Freons").

Materials of Construction: Full stainless steel construction is standard.

Safety Features: A high vapor temperature thermostat is standard. A high boiler temperature thermostat is optional and should be obtained. High and low liquid level controls are optional, as is the automatic feed pumping system. These items must be purchased in order for the still to operate safely as a continuous feed unit.

Heating and Cooling Options: Electric or steam heated units are available. Cooling is normally done by water, but a refrigeration unit is available on some of the models designed for "Freons".

Utility Requirements: 230V 3 phase or 230V single phase for electrically heated models, pressurized steam for steam heated models, cooling water, and drainage.

Remarks: Filtration systems and dessicant dryers are available if high purity solvents are required.

Available Models: Some specifications for their smaller stills are given in Table A-2.

TABLE A-2
BARON-BLAKESLEE SOLVENT STILLS

MODEL	SOLVENTS	THRUPUT	COOLING	L" x W" x H"	PRICE
NRS-60	Chlorinated	60 GPH	Water	64 x 44 x 81	$ 6,915
MRW-20	Freons	20 GPH	Water	47 x 36 x 71	$ 5,200
MRW-60	Freons	60 GPH	Water	56 x 43 x 81	$ 5,710
MRR-10	Freons	10 GPH	Refrig.	35 x 30 x 61	$ 5,250
MRR-20	Freons	20 GPH	Refrig.	40 x 43 x 73	$ 8,380
MRR-60	Freons	60 GPH	Refrig.	75 x 52 x 97	$11,940

(3) Branson Cleaning Equipment Company
Parrott Drive
Shelton, Connecticut 06484-9987
(203) 929-7301

Still Type: Continuous feed units. Designed primarily for integral use with Branson vapor degreasers, but can be used independently as well.

Solvents Designed For: The stills are not explosion proof and they operate at atmospheric pressure (no vacuum available). Therefore they can distill only nonflammable (halogenated) solvents with a boiling point lower than approximately 350°F.

Water Separator: Standard

Thruput/Capacity" Branson stills will distill waste solvents at thruputs from 8 to 96 GPH depending on the model and the solvent being distilled.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: High vapor temperature and high boiler temperature thermostats are standard on all models. A low liquid level control is also standard. A feed pump and a high liquid level control are optional and must be purchased in order to operate the still safely as a continuous feed unit.

Heating and Cooling Options: Electric or steam heated units are available. Cooling is normally done by water, but refrigeration units are available if desired.

Utility Requirements: Depending on the heating and cooling options chosen, the following many be needed: 230V 3 phase (electrically heated models), 230V single phase (steam heated models), pressurized steam, water, and drainage.

Remarks: 4 dessicant dryer is available if high purity "Freons" are required.

Available Models: Specifications and prices for some of Branson's smaller stills given in Table A-3.

TABLE A-3
BRANSON SOLVENT STILLS

	THRUPUT (GPH)					
MODEL	TCE	FREON TF	FREON TMC	COOLING	L" x W" x H"	PRICE
S110W			7.8	Water	26 x 22 x 51	$3,025
S111W	9.3	14.9		Water	26 x 22 x 51	$3,125
S120W			16.1	Water	26 x 22 x 51	$3,520
S121W	21.3	31.3		Water	26 x 22 x 51	$3,595
S110R			7.8	Refrig.	26 x 42 x 51	$5,635
S111R	9.3	14.9		Refrig.	26 x 42 x 51	$5,938
S120R			16.1	Refrig.	26 x 42 x 51	$7,435
S121R	21.3	31.3		Refrig.	26 x 42 x 51	$7,710

(4) Brighton Corporation
11861 Mosteller Road
Cincinnati, Ohio 45241
(513) 771-2300

Still Type: Continuous feed units. They make two basic stills. The first type has a flat-bottomed boiler with manual cleanout. The second type has a cone-shaped boiler bottom with scraper bars that continuously clean the boiler and discharge the sludge automatically.

Solvents Designed For: The stills are explosion-proof and are equipped with vacuum attachments. Therefore, virtually any commonly-used organic solvent with a boiling point up to 500°F can be distilled. The scraped cone bottom boilers are recommended for high soilds applications.

Water Separator: Optional ($440)

Thruput/Capacity: Brighton stills range in thruput from 7.5 to 200 GPH.

Materials of Construction: Standard material is primarily carbon steel throughout, except for copper condenser tubes. Stainless steel construction is available as an option (see Section 4.5).

Safety Features: Boiler temperature is controlled by regulating the amount of steam entering the jacket that surrounds the boiler. Boiler temperature must be monitored with the thermometer mounted on the boiler. The stills contain level controls for continuous operation.

Heating and Cooling Options: Heating is normally performed by steam using a jacket that surrounds the boiler. However, for solvents with an atmospheric boiling point over 350°F, a heat transfer fluid (oil) must be used. This requires the purchase of an optional electric fluid heating system. Condenser cooling is performed by water.

Utility Requirements: Depending on the heating and cooling options used, the following may be required: electricity, steam (100 psig), water, and drainage.

Available Models: Base prices for their smaller standard models are given in Table A-4.

TABLE A-4
BRIGHTON SOLVENT STILLS

THRUPUT (GPH)	FLAT BOTTOM	SCRAPED CONE BOTTOM
7.5	$18,230	$22,830
25	$22,870	$29,690
50	$28,950	$37,455

(5) Cardinal Corporation
P. O. Box 4234
Wilmington, DE 19807
(302) 656-9446

Still Type: Batch. Cardinal stills are unique in that the collection drum is the still pot. Waste solvent is collected in a 55-gallon steel drum. When full, the drum is placed inside the unit and an electric heater is clamped around the bottom.

Solvents Designed For: The stills operate at atmospheric pressure. They are available with or without explosion proofing. Therefore, depending upon which still is obtained, any solvent (flammable or nonflammable) with a boiling point lower than approximately 350°F can be processed.

Water Separator: Not available.

Thruput/Capacity: There are two basic models. One model (-10) can process one drum of spent solvent in an 8-hour shift. the other model (-20) can process two drums simultaneously in 8 hours, or can be run as a one drum unit.

Materials of Construction: Since the collection drum doubles as the boiler, stainless steel construction is not possible. However, since this drum is disposed of, this is not a concern.

Safety Features: A thermostat automatically turns the unit off when the vapor temperature reaches a preset limit.

Heating and Cooling Options: The stills are heated electrically and cooled by refrigeration units.

Utility Requirements: 240V, 3-phase electrical service.

Remarks: Explosion-proofing is Class I, Group D, Division 2 (See Section 4.1.1).

Available Models: Specifications and prices for Cardinal's solvent stills are listed in Table A-5.

TABLE A-5
CARDINAL SOLVENT STILLS

MODEL	DRUMS PER SHIFT	EXPLOSION PROOF	PRICE
MC-10	1	NO	$16,300
AC-10	1	YES	$16,400
MC-20	2	NO	$17,700
AC-20	2	YES	$17,900

(6) DCI Corporation
5752 West 79th Street
Indianapolis, Indiana 46268
(317) 872-6743

Still Type: DCI stills are either direct steam injection units or hybrid units that can be operated as either a direct steam injection or a steam jacket system. The stills operate on a batch basis, but are filled, turned on, and turned off automatically. This results in "semi-continuous" operation. Still bottoms are discharged automatically as well.

Solvents Designed For: The stills are explosion-proof. Direct steam injection can be used to distill virtually any immiscible solvent (see section 3.3 for a full discussion of direct steam injection). In addition, the hybrid units can be switched to convection (steam jacket) heating to distill miscible solvents. Therefore, DCI units can be used to distill virtually all the commonly used organic solvents.

Water Separator: Standard on all models.

Thruput/Capacity: Depending on the model chosen, DCI stills can operate at thruputs from 10 to 1,000 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: A boiler temperature thermostat turns the still off automatically and also triggers the automatic discharge of the still bottoms. The stills also have overflow protection (level controls) in the boiler and in the condenser.

Heating and Cooling Options: As mentioned before, heating is performed by either direct steam injection or by steam jacket (hybrid units). Cooling is performed by water.

Utility Requirements: Depending on the model purchased, the following may be required: 110V, 60 cycle power ("DG" units), 220V 3 phase power ("D1" units), steam, compressed air (80 psi for all models), water, drainage.

Remarks: The smaller stills are available with carbon steel construction at lower cost (see Section 4.5).

Available Models: Some specifications and base prices for DCI's smaller units are given in Table A-6.

TABLE A-6
DCI SOLVENT STILLS

MODEL	THRUPUT (GPH)	L" x W"	EXPLOSION PROOF	NON-EXPLOSION PROOF
DIRECT STEAM INJECTION ONLY:				
DG-10-SST	10	58 x 43	$18,840	$16,275
DG-25-SST	25	58 x 43	$29,395	$25,545
D1-50-SST	50	54 x 56	$33,745	$29,240
HYBRID UNITS:				
DG-10-SST-HY	10	58 x 43	$22,230	$20,665
DG-25-SST-HY	25	58 x 43	$34,745	$30,895
D1-50-SST-HY	50	54 x 56	$43,600	$39,090

(7) Disti Incorporated
131 Prince Street
New York, New York 10012
(212) 505-0677

Still Type: Batch, filled through top cover.

Solvents Designed For: Disti stills are explosion proof and are available with vacuum attachments. As a result, virtually all commonly-used organic solvents can be distilled.

Water Separator: Optional

Thruput/Capacity: Boiler capacities (batch sizes) vary from 7 gallons to 1,000 gallons. Thruputs vary from 3 GPH to 300 GPH.

Materials of Construction: Standard construction is with mild steel, but stainless steel is available as an option (see Section 4.5).

Safety Features: A double safety thermostat shuts the unit down when the boiler temperature reaches a pre-set limit. This feature is used as an automatic turn-off system.

A flow switch ensures that the stills will not operate unless cooling water is flowing through the condenser.

Heating and Cooling Options: Heating is performed by an electrically heated heat transfer fluid (hot oil) jacket. Cooling is performed by water.

Utility Requirements: The units discussed here require three phase AC power of any voltage. Cooling water and drainage are also required.

Remarks: Disti stills are manufactured in West Germany by a company named D. W. Renzmann.

Available Models: Specifications and prices for some of Disti's stills are listed in Table A-7.

TABLE A-7
DISTI SOLVENT STILLS

MODEL	CAPACITY (GAL)	THRUPUT (GPH)	L" x W" x H"	BASE PRICE
DW-25	7	3-5	37 x 26 x 35	$ 5,700
DW-50	.5	5-8	51 x 27 x 47	$ 9,850
DW-100	30	8-16	55 x 28 x 50	$13,800
M2ON	60	10-20	55 x 53 x 65	$17,850

Options For "DW" Series Skills:

Vacuum unit - $2,500
Water separator - $1,650
Combination vacuum/water separator - $3,300
Stainless steel construction - $3,900

Options For Model MN20:

Vacuum unit - $2,890
Water separator - $1,650
Combination vacuum/water separator - $3,690
Stainless steel construction - $5,600

(8) Finish Engineering Company
Erie, Pennsylvania

Government Distributor:
Extratec Corporation
18220 Allwood Terrace
P.O. Box 533
Olney, Maryland 20832
(301) 924-5150

Still Type: Batch. Filled through top cover.

Solvents Designed For: Finish stills are explosion proof and are available with vacuum units. Therefore, they can be used for recycling any solvent (flammable or nonflammable) with a boiling point up to 500°F (virtually all organic solvents).

Water Separator: Not available.

Thruput/Capacity: The stills are basically designed to process one batch per shift. Batch sizes range from 15 to 500 gallons. The two most popular still sizes are 15 and 55 gallons.

Materials of Construction: The boilers are Teflon-coated, stainless steel, which means that still bottoms will not stick to the sides or the bottom. All other parts are stainless steel.

Safety Features: A thermostat shuts the unit off when the boiler reaches a pre-set temperature. Redundant temperature controllers disallow any single spot form reaching 365°F.

Heating and Cooling Options: Most Finish stills are electrically heated. The 55-gallon capacity still is available with steam heat (a portable boiler package is available). Cooling is performed with water.

Utility Requirements: Depending upon the still obtained, the following may be required: 110V power, 220V power, steam, cooling water, and drainage.

Remarks: A small steam boiler system is available if steam heating is desired but in-house steam is not available.

Available Models: Finish Engineering currently has a GSA contract for it's solvent stills. The stills are covered under FSC Class 6640 and contract number GS-00F-79500, which expires 1 August 1986. Special item numbers, specifications, and GSA prices for Finish Engineering's "LS" series stills are given in Table A-8.

TABLE A-8
FINISH ENGINEERING STILLS

SPECIAL ITEM NO.	MODEL	CAPACITY (GAL)	HEATING	L" x W" x H"	PRICE
0517	LS-jr	3-5	Elec		$ 2,845
7011	LS-15	15	Elec.	30 x 44 x 36	$ 5,344
7257	LS-15V				
	w/Vacuum	15	Elec.	30 x 66 x 39	$ 9,305
7259	LS-55	55	Elec.	34 x 56 x 69	$13,252
7260	LS-55V				
	w/Vacuum	55	Elec.	34 x 78 x 60	$19,047
9831	LS-55-ST	55	Steam	34 x 56 x 65	$18,895
9831	LS-55-ST				
	w/Vacuum	55	Steam	34 x 78 x 65	$24,690

(9) Hoyt Corp.
Forge Road
Westport, Massachusetts 02790
(800) 343-9411
in Ma. (617) 636-8811

Still Type: Continuous feed stills. Boilers have scraper-agitator bars for removing solids from the boiler walls. Still bottoms are discharged automatically.

Solvents Designed For: Explosion-proofing is available. The stills operate at atmospheric pressure (no vacuum available). Therefore, any organic solvent (flammable or nonflammable) with a boiling point lower than approximately 350°F can be distilled.

Water Separator: Optional.

Thruput/Capacity: Hoyt Solvo-Salvagers will distill solvents at a rate of 4 to 8 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: A high boiler temperature thermostat is standard. Liquid level controls are also standard and the unit will automatically shut down for lack of feed solvent. The still will not operate without the condenser cooling water flowing or with a low thermal oil (heating medium) level.

Heating and Cooling Options: Heating is performed by a heat transfer fluid (hot oil) jacket. The oil is heated electrically. Cooling is performed by water.

Utility Requirements: 220V electricity, 2 gallons per minute of cooling water, and drainage are needed.

Available Models: The Solvo-Salvager is available in one basic model.

TABLE A-9
HOYT CORPORATION STILLS

MODEL	THRUPUT	L" x W" x H"	PRICE
EP8	4-86PH	30 x 30 x 92	$14,500

(10) Lenepe Equipment Co.
P. O. Box 285
Manasquan, New Jersey 08736
(201) 681-2442

Still Type: Continuous Feed.

Solvents Designed For: The stills are not explosion proof and they operate at atmospheric pressure. Therefore, they can be used to distill nonflammable (halogenated) solvents with a boiling point below approximately 350°F.

Water Separators: Standard.

Thruput/Capacity: Depending upon the unit obtained, Lenepe stills can recycle solvent at rates from 1.5 GPH to 150 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: High vapor temperature and high boiler temperature thermostats are standard. A low liquid level control switch is also standard. An automatic solvent level control and a feed pumping system are optional and should be obtained in order to safely operate the stills as continuous feed units.

Heating and Cooling Options: Heating on all models is electric. Cooling is performed by either water or by refrigeration units.

Utility Requirements: Electricity is required, as well as, water and drainage (water cooled models).

Remarks: A dessicant dryer assembly is available as an option for situations when extraction of solvent components by water may occur.

Available Models: Specifications and base prices for some of Lenepe's smaller models are listed in Table A-10.

TABLE A-10
LENEPE SOLVENT STILLS

MODEL	THRUPUT (GPH)	COOLING	L" x W" x H"	PRICE
AW2	3-10	Water	20 x 26 x 38	$3,495
AR2	3-10	Refrig.	20 x 41 x 38	$4,945
BW6	14-40	Water	35 x 26 x 49	$6,935
BR6	14-40	Refrig.	35 x 58 x 49	$9,685

(11) Phillips Manufacturing Co.
7334 North Clark Street
Chicago, Illinois 60626
(312) 338-6200

Still Type: Continuous feed.

Solvents Designed For: The stills are not explosion-proof and they operate at atmospheric pressure (no vacuum attachment is available). Therefore, Phillips stills are designed to recycle nonflammable (halogenated) solvents with a boiling point below approximately 350°F.

Water Separation: Standard.

Thruput/Capacity: Phillips stills vary in thruput from 1 to 1,000 GPH.

Materials of Construction: Standard stills are manufactured with galvanized mild steel. Stainless steel construction is optional.

Safety Features: All models are equipped with automatic level controls. Electric models are equipped with a boiler temperature thermostat.

Heating and Cooling Options: Phillips' stills are heated by steam, electricity,
or gas. Cooling is normally performed by water, but refrigeration units are available as an option.

Utility Requirements: Depending on the model obtained, the following may be required: electricity, steam, gas, water, and drainage.

Available Models: Specifications and prices for some of Phillips' smaller stills are listed in Table A-11. The prices listed include the extra cost for stainless steel construction.

TABLE A-11
PHILLIPS SOLVENT STILLS

MODEL	(GPH)	HEATING	L" x W" x H"	PRICE
RS-3	3	Elec.	26 x 21 x 49	$2,121
RS-10	10	Steam	30 x 28 x 65	$4,753
RS-10	10	Elec.	30 x 28 x 65	$4,973
RS-10	10	Gas	30 x 28 x 65	$5,341
RS-50	50	Steam	48 x 40 x 84	$6,378
RS-50	50	Elec.	48 x 40 x 84	$7,822
RS-50	50	Gas	48 x 40 x 84	$8,202

(12) Progressive Recovery Inc.
1976 Congressional Drive
St. Louis, Missouri 63146
(314) 567-7963

Still Type: Batch. "SC" models have flat bottomed boilers. "LSR" models have a conical shaped bottom that is continually scraped for high solids applications.

Solvents Designed For: PRI stills are explosion-proof, and vacuum assist is available on all models except the SCjr. Therefore, the stills are capable of recycling any solvent with a boiling point up to 500°F (virtually all organic solvents).

Water Separator: Optional.

Thruput/Capacity: PRI stills are available with capacities from 5 to 710 gallons. Thruputs range from 1 to 260 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: The electrical heating elements are controlled by a double safety thermostat. A flow switch ensures that the unit will not operate for lack of cooling water. A vapor temperature thermostat in the condenser provides backup protection to this switch.

Heating and Cooling Options: Heating is performed by an electrically heated heat transfer fluid (hot oil) jacket or a steam jacket. The stills are cooled by water except for the SCjr model, which is air cooled.

Utility Requirements: Either 220V power, 440V power, or steam is required, along with water and drainage.

Available Models: Specifications and base prices for some of PRI's smaller stills are listed in Table A-12.

TABLE A-12
PRI SOLVENT STILLS

MODEL	CAPACITY (GAL)	THRUPUT (GPH)	HEATING	PRICE
SCjr	5	1-2	Electric	$ 4,745
SC50	35	4-6	Electric	$ 9,675
SC100	35	7-9	Electric	$11,895
SC200	60	12-17	Electric	$17,195
LSR-8.5E	55	10-12	Electric	$44,965
LSR-8.5	55	12-15	Steam	$44,965

The cost of a vacuum assist unit for any of PRI's stills is approximately $3,000.

(13) Randall Manufacturing Company Inc. (RAMCO)
32 Montgomery Street
Hillside, New Jersey 07205
(201) 687-6700

Still Type: Continuous feed.

Solvents Designed For: The stills are not explosion-proof and they operate at atmospheric pressure (no vacuum is available). Therefore, they are designed to distill nonflammable (specifically halogenated) solvents with a boiling point lower than approximately 350°F.

Water Separator: Standard.

Thruput/Capacity: Ramco stills are available with thruputs ranging from 25 to 200 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: Standard safety features include a high vapor temperature thermostat and a high boiler temperature thermostat. A flow sensing switch shuts the unit down if water is not flowing through the condenser. The boiling chamber has a level control that shuts the unit down if the solvent level is too low.

Heating and Cooling Options: Ramco stills are available in either electric or steam heated models. Cooling is performed by water.

Utility Requirements: Depending on the heating option chosen, the stills may require electricity or steam, along with cooling water and drainage.

Available Models: Specifications and base prices for some of Ramco's smaller stills are given in Table A-13.

TABLE A-13
RAMCO SOLVENT STILLS

MODEL	THRUPUT (GPH)	HEATING	L" x W" x H"	PRICE
R25	25	Steam	66 x 46 x 78	$6,975
R25	25	Electric	66 x 46 x 78	$7,496
R50	50	Steam	82 x 52 x 78	$7,719
R50	50	Electric	82 x 52 x 78	$8,547

(14) Recyclene Products Inc.
1910 Trade Zone Blvd.
San Jose, California 95131
(408) 945-8600

Still Types: Batch. Disposable bags are used to line the boiler during operation. When the batch is complete, the bag (which now contains the still bottoms) is disposed. An automatic feed system is available to pump the solvent into the boiler.

Solvents Designed For: Recyclene stills are explosion proof. They operate at atmospheric pressure (no vacuum attachment is available). Therefore, the stills can be used to recycle any solvent (flammable or nonflammable) with a boiling point lower than approximately 350°F.

Water Separator: Not available.

Thruput/Capacity: Recyclene stills are available with boiler capacities of either 20 gallons or 35 gallons. Thruput range from 0.5 to 35 GPH.

Materials of Construction: Stainless steel construction is standard except for the condenser, which is made of a copper-nickel alloy.

Safety Features: A double safety thermostat shuts the unit off automatically when the boiler temperature reaches a preset limit. A condenser overheat thermostat shuts the still down if the cooling water is not running. A safety interlock prevents the opening of the boiler lid while the system is running or is hot. A high liquid level control prevents over-filling of the boiler if the auto-feed option is chosen.

Heating and Cooling Options: Heating is performed by an electrically heated heat transfer fluid (hot oil) jacket. The stills are cooled by water.

Utility Requirements: Recyclene stills require 240V power, cooling water, drainage, and 60 to 110 psi compressed air (the still lid is raised pneumatically).

Remarks: Recyclene stills were formerly sold under the name of Zerpa Industries.

Available Models: Recyclene currently has a GSA contract for its solvent stills. The stills are covered under FSA Class 4940 and contract number GS-007-79421 which expires 23 May 1987. Special item numbers, specifications and GSA prices for Recyclene stills are listed in Table A-14.

TABLE A-14
RECYCLENE SOLVENT STILLS

SPECIAL ITEM NO.	MODEL	CAPACITY (GAL)	THRUPUT (GPH)	L" x W" x H"	PRICE
8051	RS-20	20	0.5-3	30 x 43 x 43	$11,077
8137	RS-35	35	4-12	51 x 51 x 50	$16,514
8138	RS-35 W/Auto-fill	35	4-12	51 x 51 x 50	$21,147
8139	RX-35	35	10-35	51 x 51 x 50	$21,399
8149	RX-35 W/Auto-fill	35	10-35	51 x 51 x 50	$26,031
8141	Options and Accessories				

(15) Unique Industries, Inc.
11544 Sheldon Street
Sun Valley, California 91352
(213) 875-3810

Still Type: Continuous feed.

Solvents Designed For: The stills are not explosion proof and they operate at atmospheric pressure (no vacuum is available). Therefore, they can distill only nonflammable (halogenated) solvents with a boiling point below approximately 350°F.

Water Separator: Standard

Thruput/Capacity: Vapo-Kleen stills can recycle solvents at rates ranging from 12 GPH to 110 GPH.

Materials of Construction: Full stainless steel construction is standard.

Safety Features: High vapor level and high boiler temperature thermostats are standard. Automatic liquid level controls are also standard.

Heating and Cooling Options: The stills are normally heated electrically. Steam or gas heated models can be custom built at a higher cost. Cooling is performed by water or refrigeration units.

Utility Requirements: 240V, 3-phase power is required along with possibly steam, water, and drainage.

Available Models: Specifications and base prices for the smaller Vapo-Kleen stills (electrically heated) are given in Table A-15.

TABLE A-15
VAPO-KLEEN SOLVENT STILLS

MODEL	THRUPUT (GPH)	COOLING	L" x W" x H"	PRICE
1100-10W	12	Water	43 x 38 x 59	$ 5,720
1100-10RA	12	Refrig.	56 x 38 x 59	$ 8,600
1100-20W	21	Water	40 x 37 x 62	$ 7,500
1100-20RA	21	Refrig.	70 x 37 x 62	$10,750
1100-30W	41	Water	50 x 41 x 62	$ 8,500
1100-30RA	41	Refrig.	87 x 41 x 62	$12,750

(16) Venus Products Inc.
1862 Ives Ave.
Kent, WA 98032
(206) 854-2660

Still Types: Batch. Venus stills have hoses with fittings that connect directly to 55-gallon drums of waste solvent. The solvent is automatically pumped into the unit, distilled, and the clean solvent is deposited into a clean drum. There are two basic units (the SR-5 and the SR-20).

Solvents Designed For: The stills are explosion proof and can, therefore, be used for both flammable and nonflammable solvents. They operate at atmospheric pressure (no vacuum attachment is available). They are designed to distill solvents with a boiling point up to 210°F.

Water Separator: Not available.

Thruput/Capacity: Model SRS-5 has one hose for a waste solvent drum and one hose for a clean drum. It is designed to process this one drum in an 8-hour shift (a thruput of approximately 7 GPH). Model SRS-20 has four hoses for waste solvent drums and four hoses for clean drums. It is designed to automatically process these four drums in an 8-hour shift (a thruput of approximately 27 GPH).

Materials of Construction: Model SR-5 comes standard with mild steel construction. Model SR-20 comes standard with aluminum construction. Stainless steel construction is available on both units as an option.

Safety Features: Standard safety features include a vapor temperature thermostat and a boiler temperature thermostat. The unit is also shut down if the heat transfer fluid level is too low.

Heating and Cooling Options: Heating is performed by an electrically heated heat transfer fluid (hot oil) jacket or electric immersion heaters. Model SRS-5 is cooled by water. Model SRS-20 is cooled by a refrigeration unit mounted on top of the still.

Utility Requirements: The stills require 240V power, compressed air (to drive the pumps), cooling water (Model SR-5), and drainage.

Remarks: Venus stills are designed to be located outdoors. Roofing is provided with the units.

Available Models: Specifications and base prices for Venus' two basic stills are listed in Table A-16.

TABLE A-16
VENUS SOLVENT STILLS

MODEL	BOILER CAPACITY(GAL)	THRUPUT (DRUMS/SHIFT)	L" x W" x H"	PRICE
SRS-5	15	1	44 x 44x 168	$11,000
SRS-20	600	4	44 x 56 x 168	$21,000

(17) Westinghouse Electric Corp.
Industrial Equipment Division
Route 32
P.O. Box 300
Sykesville, Maryland 21784
(301) 795-2800

Still Type: Continuous feed.

Solvents Designed For: The stills are not explosion proof and they operate at atmospheric pressure. Therefore, they are designed to distill nonflammable (halogenated) solvents with a boiling point lower than approximately 350°F.

Water Separator: Standard.

Thruput/Capcity: Capacities range from 18 to 85 gallons with thruputs from 15 to 55 GPH.

Materials of Construction: Stainless steel construction is standard.

Safety Features: A boiler thermostat protects against excessive temperature in the boiler liquid. A vapor temperature thermostat in the condenser shuts the unit down if cooling is inadequate. Level controls automatically maintain the solvent level in the boiler.

Heating and Cooling Options: The stills are heated electrically and cooled by either water or a refrigeration unit (optional).

Utilitiy Requirements: Standard requirements are 220/440V 3 phase power, cooling water, and drainage.

Available Models: Specifications and prices for Westinghouse stills are listed in Table A-17.

TABLE A-17
WESTINGHOUSE SOLVENT STILLS

MODEL	THRUPUT (GPH)	L" x W" x H"	PRICE
SRS15	15	31 x 39 x 56	$ 6,680
SRS30	30	47 x 47 x 72	$ 9,880
SRS60	55	51 x 50 x 92	$14,165